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PHYSICO-CHEMICAL INVESTIGATIONS IN THE PYRIDINE SERIES.

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The idea which led us to undertake this work was the desire to ascertain in how far the regularities in the increase in the heats of combustion and of formation, and the determined constants for the molecular heat of evaporation, which had been observed between homologues in the fatty and in the aromatic series would be found to apply to the pyridine series.

For this purpose we undertook to prepare considerable quantities of as pure substances as could possibly be obtained, and with these to carry out investigations with the above objects in view.

This investigation eventually led us further than had been originally intended, since relations between the compounds studied appeared during the course of the work of such interest as to make it desirable not merely to confine the investigation to a study of the heat relations but to include an electrochemical study as well.

Preparation of the Pure Bases.

This has proved by no means a light task and has occupied

by far the major portion of the whole time devoted to the research. Although Ladenburg[1] and his pupils, as well as Schwarz,[2] Stoehr,[3] and others had previously prepared and described some of the properties of these bases and had outlined the general methods employed for their purification, they had occasion to prepare only a very few grams ; it proved a much more difficult task to obtain larger quantities in a state of purity such as was required for this investigation. Moreover, the properties as published by these investigators do not entirely agree in all respects, indicating possible sources of impurity in some cases.

For this reason, and that it may be seen what the condition of purity of the substances used by us was, we give here in some detail the methods employed for this purpose. These are essentially similar to those described by the investigators mentioned, differing in some minor particulars only, which will be mentioned in the proper connection. It was found that the mercuric chloride double salt was in most cases best suited to the separation and purification of the bases, being very insoluble and crystallizing well, entailing minimum loss during the repeated recrystallizations necessary, but possessing, on the other hand, the disadvantage that, on account of the high specific gravity and marked insolubility, the difficulty of working with large quantities is greatly increased.

The pyridine used was at first purified by conversion into the ferrocyanide and into the zinc salt ; it was, however, later found possible to obtain pyridine from Kahlbaum possessing a high degree of purity, such that a perfectly satisfactory product could be obtained from it by fractionation, after drying over caustic potash. While for most of the experiments the pure base obtained from the ferrocyanide was used, a comparison of the heats of combustion, as given in Table I., will show that the Kahlbaum product was practically identical in its properties with that prepared by us.

The pyridine thus obtained possesses a not unpleasant odor, boils constantly at 115°.2 C. at 760 mm. and 0° C., the ther-

[1] Ann. Chem. (Liebig), **247**, 7 (1886).
[2] Ber. d. chem. Ges., **24**, 1676 (1891).
[3] J. prakt. Chem., [2], **48**, 20 (1892).

mometer entirely in the vapor. It is strongly refractive and has a density at 15° C., calculated to water at 4° C., of 0.989305.

Although Kahlbaum furnished us also with a quite pure α-picoline, careful tests showed that it still contained minute traces of other bases. We deemed it advisable, therefore, to subject it to further purification, and for this purpose transformed it into the mercuric chloride double salt, as described by Ladenburg, and recrystallized this from hot water containing a small amount (2 to 3 per cent) of dilute hydrochloric acid.

The purification of this salt can be easily accomplished by adopting the following procedure: After preparing a very concentrated solution by the aid of heat, filter rapidly through a folded filter, using a stemless funnel for the purpose; any crystals formed are again brought into solution, and the vessel set aside until crystallization sets in. The α-picoline salt, on account of its great insolubility, soon begins to separate out in large diamond-shaped, striated prisms, which frequently attach themselves together, building up long, lance-shaped needles, terminated by one of the diamond-shaped crystals. After the greater part—but not all—of the α-picoline salt has separated out, minute, iridescent flakes are formed, settling slowly; if at this point the mother-liquid be poured off and the operation of dissolving, recrystallizing, and pouring off be repeated, perfectly pure mercuric chloride double salt, of composition $C_6H_7N.HCl.2HgCl_2$, melting sharply and constant at 153° to 153°.5,[1] can be obtained in two to three crystallizations.

To obtain the base from this it was decomposed with double the calculated amount of sodium hydroxide in concentrated solution, the whole brought into a copper flask, and distilled over a free flame until the greater part of the liquid had distilled off, then in a current of steam, until the distillate no longer had the characteristic odor of the base and exhibited only a very faint alkaline reaction with litmus. The base was then separated from the distillate by the addition of solid caustic potash, with cooling, until a very concen-

[1] For comparison we give the values of other observers: Ladenburg and Lange, 154°.

trated potassium hydroxide solution was obtained. The base separated as a light, transparent, oily layer at the top and was removed by means of a separatory funnel. The potassium hydroxide solution was extracted with ether and, after distilling off the ether at the lowest possible temperature (the last portions best by means of a slow current of air), the entire amount was thoroughly dried over solid potassium hydroxide and distilled. It showed a constant boiling-point 128°.8 C. (128°.7 and 128°.9 for two different preparations) at 760 mm. and 0° C.,[1] with the mercury entirely in the vapor. We obtained in this way, partly by repeated fractionation of a mixture of pyridine bases and use of the fraction boiling between 128° to 133°, partly starting from the Kahlbaum "pure" α-picoline, a total of 115 grams with the above boiling-point.

This α-picoline is a clear, transparent liquid, with a very marked characteristic, pyridine-like odor and a strong refractive action upon light; it volatilizes markedly and has a strong tendency to absorb water, so that it must be kept in well-stoppered flasks over solid caustic potash; it attacks cork, rubber, and other organic substances quite markedly. The density at 15° C., reduced to water at 4° C., is 0.94972.

The β-picoline which we used in our subsequent experiments was obtained from three separate sources: One portion prepared synthetically by ourselves, using Stoehr's[2] method; a second portion, which had been previously prepared by him, was received from Mr. E. Stebler, of this laboratory, while for the major fraction we are indebted to the kindness of Prof. Stoehr himself. To both of these gentlemen we here take the opportunity of expressing our sincerest thanks.

All of these were received in the raw condition and were subsequently purified. The raw base contains a large number of other substances, from which it is not easy to separate it in pure condition. The method which we made use of for this purpose was essentially that described under α-picoline, though in this case the operation required closer attention and

[1] Ladenburg, 129°; Lange: Ber. d. chem. Ges., 18, 3436, 129° to 130°; Kahlenberg: J. phys. Chem., 3, 254, 129° at 745 mm. The latter used Schuchardt's a-picoline, without further purification.

[2] A later portion was worked over according to a method privately communicated by Prof. Stoehr, which materially lessened the time of the operation.

many more recrystallizations than was the case with the α-compound. On account of the number of impurities present, all of which form difficultly soluble double chlorides with mercury, differing very little in point of solubility from that of the β-salt, the crystallizations had to be controlled by means of the magnifying glass, and only when an absolutely uniform product was obtained were we satisfied as to its purity. This was rendered the more difficult on account of two factors which affect the result: the β-salt does not show so marked a crystal habit as the α-salt, but varies considerably with the degree of concentration and the nature of the impurities present. Generally it is obtained in the form of long, prismatic needles, but can also be obtained in thin, friable leaflets, apparently formed by the clustering of the needles; it was also found impossible to obtain a product crystallized from acidulated water with a constant melting-point, although microscopic examination showed it to be uniform in character. We found, however, that on recrystallizing from hot alcohol (80 to 90 per cent), in which it is quite easily soluble (though only slightly so in the cold) a product was obtained which melted sharply at 146° C.[1]

The difficulty in obtaining a salt of constant melting-point from aqueous solutions is apparently due to a partial hydrolytic dissociation of the salt by the water present. β-picoline belongs to a class of weak bases and its salts react acid toward indicators, all giving the characteristic odor of the base. In the case of the double salt with mercuric chloride, although we constantly worked with acidulated solutions, the odor of the base is quite pronounced. If the solid salt be brought into water heated nearly to the boiling-point, with the flame still under the vessel, it in part dissolves at once, but a considerable portion sinks to the bottom and forms an oil which only slowly dissolves, the solution meanwhile giving a very pronounced odor of the base. If the liquid be poured off from the oil, the latter instantly solidifies to a hard cake which is much more difficultly soluble than the original crystallized salt, and which shows a markedly different melt-

[1] Ladenberg, 143°; Schwars, 147° to 149°; Stoehr, 146°.

ing-point from the salt itself. Considerable variations in melting-point were observed with the various fractions, but all showed virtually the same when recrystallized from moderately strong alcohol. The same observation was made with the γ-picoline compounds, being even more marked in that case, since γ-picoline is a somewhat weaker base than β-picoline.

The β-picoline obtained from the mercury salt by distilling with sodium hydroxide, separating with caustic potash, and drying over solid potassium hydroxide, boiled at 143°.4 C. at 760 mm. and 0° C.,[1] with the mercury entirely in the vapor of the boiling liquid. It has a much more agreeable ethereal odor than α-picoline, and, like the latter, has a strong refractive action on light. The density at 15° C., calculated to water at 4° C., is 0.96134.

As the starting-point for the preparation of the γ-picoline we made use of a mixture of bases furnished by Kahlbaum. This was subjected to repeated fractionation, and, eventually, the fraction distilling between 128° and 133° was used in the preparation of α-picoline, as already mentioned, while the fraction 140°–146° was used for the preparation of the γ-picoline. Unfortunately, an accident deprived us of a considerable quantity of the rectified raw base, which prevented the subsequent investigations being carried out in their entirety upon this member of the picoline group.

To obtain the γ-picoline, the fraction 140°–146° was converted into the hydrochloride and fractionally precipitated, as described by Ladenburg, Mohler, etc., with mercuric chloride. The salt obtained was very impure, but was separated by subsequent recrystallizations from acidulated hot water into three principal portions: one consisting of broad leaflets, constituting about one-half of the total, and which, after several recrystallizations, melted constant at 164° to 165°; a second portion, crystallized in small, thin leaflets, gave a melting-point of 186°.5 to 187°.5, and corresponds both in crystal form and melting-point to α,α'-lutidine, while the third portion containing the γ-picoline salt mostly, crystallized as long, thin

[1] Ladenburg, 142° to 144°; Schwarz, 143°.5; Stoehr, 143° to 143°.2 at 750 mm.

needles. It was found even more difficult to obtain a salt of constant melting-point in this case than in the case of the β-compound, and the phenomena noted there were observed in a much more marked degree: the formation of larger quantities of the oil, a more noticeable odor of the base, and a greater divergence of the melting-point from a constant. The latter fact was also noted by Mohler,[1] who states that he succeeded in bringing the melting-point from 130°, that of the original salt, to 150°, by repeated recrystallizations. This and later observations made with other salts of γ-picoline, notably with the picrate, as well as a consideration of the widely diverging values found by various investigators, leads to the conclusion that γ-picoline is a very weak base, and that hydrolytic dissociation is the cause of these discrepancies. Recrystallization from alcohol materially reduced this, though apparently not completely (the alcohol used was only about 85 to 90 per cent). The melting-point of the salt recrystallized from alcohol was 124° to 128° and showed no perceptible change on repeating the crystallization. The base obtained from this had the boiling-point 143°.1 C. at 760 mm. and 0° C.[2] The density at 15° C., calculated to water at 4° C., is 0.95714.

THERMOCHEMISTRY OF THE PYRIDINE BASES.

Although a few determinations of this sort have been made by other investigators, more especially with pyridine and α-picoline, the results obtained by the various observers are not in sufficiently close agreement to render redeterminations of these values superfluous. We have therefore undertaken to make as far as possible, with the material in hand, a complete thermochemical study of the pyridine bases. Comparison of the results obtained by us with those of other observers will be made under each group of investigations.

The room in which the determinations were made was one which had been specially constructed and arranged for such purposes, lying in an underground cellar towards the north, so situated that no direct sunlight could enter, and provided

[1] Ber. d. chem. Ges., **21**, 1010 (1888).

[2] Given as 142°.5 to 144°.5, Ladenburg; 144° to 145°, Lange; 142° to 144°, Behrmann and Hoffmann.

with double walls, doors, and windows. The temperature was kept constant at 15° C. by means of a heater provided with a regulating device and a sensitive thermometer, which showed almost no appreciable deviation at any time during the investigations. All liquids were kept in the room for a long time before use, that they might be of uniform temperature, and all the usual precautions necessary to such work were carefully observed.

This part of the investigation may be classified under the following heads: Heats of combustion, of formation (calculated from the former), specific heats, heats of vaporization, and heats of neutralization. Each will be considered separately.

Heats of Combustion.

These were determined in a Mahler bomb of about 300 cc. content, in oxygen compressed to 25 atmospheres. The arrangement and construction of the entire apparatus—with the exception of the bomb itself—as well as the general method of the experiments, was as nearly as possible that described by Stohmann.[1] The thermometer used was one of the Beckmann type especially prepared for us by Goetze, in Leipzig, accurately calibrated before use and compared to a normal thermometer, which, in turn, had been tested against an air thermometer. The scale was divided into hundredths of a degree, and by means of a strong magnifying glass provided with a horizontal fiber in the eye-piece and so attached to the thermometer stem that it could readily be slid up or down without disturbing the horizontal position of the fiber, the estimation of the thousandths could be made with a moderate degree of certainty.

Since we had here to deal with extremely volatile substances whose heats of combustion were to be determined in the liquid state, it became necessary to devise an apparatus in which the combustions, as well as the weighings, could be made without any appreciable amount of vaporization taking place. This was accomplished by the use of the crucible shown in cross-section in the accompanying figure. The entire apparatus

[1] J. prakt. Chem., [2], 39, 503 (1889).

is of platinum and consists of the crucible *A*, the upper part of which is conical in shape, and a similarly conical-shaped ring *B*, made of stout platinum with an ear-piece at *c*, for handling. The crucible and ring are ground to fit closely, and by means of a brass form, into which the crucible fits, and a plunger, the two can be made to fit without difficulty and without distortion. Thin films of denitrated cellulose were used as covers, and, after the liquid was brought into the tared crucible, the cellulose film, the weight of which had been previously determined, was placed over it and the ring centered and pressed into place. If the film is not so thick that the folds produced on pushing in the ring prevent the latter from fitting the crucible closely, a very satisfactory closure can be obtained, although a noticeable loss in weight takes place at first until the film becomes saturated with the vapors of the liquid, after which it decreases to a minimum, rarely amounting to more than 0.0002 to 0.0003 gram per half hour;[1] since the time required between the final weighing and the beginning of the ensuing combustion rarely exceeded ten minutes, the error produced from this cause is practically negligible. It was further demonstrated by repeated experiments that in the compressed oxygen virtually no loss due to evaporation of liquid ensued.

No difficulty was experienced in igniting the substance if the coil of iron wire used as fuse be made to touch the cellulose. Under these conditions the heated particles of the iron oxide set fire at once both to the film and the substance, and with this form of crucible the time required to communicate the total heat to the water of the calorimeter, using 0.6 to 0.8 gram substance, was rarely more than three to four minutes. Often a thin layer of unburned carbon from the film was found at the end of the experiment between the collar and the crucible; the weight of this was afterwards determined—it varied usually between 0.0002 to 0.0008 gram—and brought

[1] α-Picoline seems to have a much more marked tendency to evaporate through the film than any of the others. It will be observed in the tables which follow that the heat values show a wider divergence from each other, probably because of this.

into the final correction, as was also the heat due to the combustion of the cellulose, the iron wire used for igniting, and the nitric acid formed by the burning of the nitrogen contained in the air originally in the bomb. The latter was absorbed in a measured quantity of water placed in the bottom of the bomb and determined by titration.

The water value of the solid parts of the apparatus was determined by burning weighed quantities of substances whose heats of combustion were accurately known.[1] For this purpose, carefully purified benzoic acid[2] and camphor[3] were made use of. These gave, as the mean of eight determinations, 389.1 grams; the calculated value, using the weights and specific heats of the component parts was 389.2 grams. The agreement is of a very satisfactory character.

The weighed substance having been introduced into the bomb, and the latter filled with compressed oxygen, it was placed in the calorimeter, containing approximately 3 liters of water, the stirring apparatus set in motion, and the whole left for a time (about five minutes) to come to a uniform temperature. A number of readings of the thermometer were then taken from minute to minute until the rate of change had become uniform, when ignition was produced by means of an electric current from a storage battery. The subsequent rise in temperature is rapid, requiring rarely more than three to four minutes to attain the maximum, after which it slowly sinks. The temperature readings of the after-period were also taken from minute to minute until the change became constant, and the corrected temperature was then calculated according to the following equation:[4]

$$\Sigma \Delta t = \frac{v-v'}{\tau'-\tau}\left(\sum_{1}^{n-1}\theta_r + \frac{\theta_n+\theta_1}{2} - n\tau\right)-(n-1)v.^{5}$$

[1] Berthelot: Traité pratique de Calorimétrie Chimique, p. 145; and Stohmann: Ber. d. math.-phys. classe de Kgl. Säch. Gesell., (1893), p. 606.

[2] 6322.3 cal. Stohmann; 6322.1 cal. Berthelot.

[3] 9291.6 cal. Stohmann; 9288.0 cal. Berthelot.

[4] Stohmann, Kleber, and Langbein: *Loc. cit.*, p. 518.

[5] This formula differs slightly from the Regnault-Pfaundler correction formula (Pogg. Ann., **129**, 102) in that the value $\sum_{1}^{n-1}\theta_r$ contains a special factor $\frac{\theta_n-\theta_1}{9}$. This added factor has been determined experimentally by Stohmann and applies only to this type of apparatus. It is due to the fact that during the first minute of combustion about 94 per cent of the total heat given up is communicated to the calorimeter, and therefore the mean temperature change does not apply.

Here, n, n_1, and n_2 = the number of observations taken during the combustion period, the fore-period, and the after-period, respectively.

$\tau_1, \tau_2, \tau_3 \ldots \tau_{n_1}$ = the successive temperature readings during the fore-period from minute 1 to minute n_1.

$\tau'_1, \tau'_2, \tau'_3 \ldots \tau'_{n_2}$ = the corresponding values during the after-period from minute 1 to minute n_2.

$v = \frac{\tau_{n_1} - \tau_1}{n_1 - 1}$ = the average change per minute during the fore-period.

$v' = \frac{\tau'_{n_2} - \tau'_1}{n_2 - 1}$ = the average change per minute during the after-period.

$\tau = \frac{\tau_1 + \tau_2 + \tau_3 + \ldots + \tau_{n_1}}{n_1}$ = average temperature of the fore-period.

$\tau' = \frac{\tau'_1 + \tau'_2 + \tau'_3 + \ldots + \tau'_{n_2}}{n_2}$ = average temperature of the after-period.

$\theta_1, \theta_2, \theta_3 \ldots \theta_n$ = the temperature readings during the combustion, until the maximum is reached, and the temperature either remains constant or, as is more commonly the case, begins to fall.

$\sum_1^{n-1} \theta r = \theta_1 + \theta_2 + \theta_3 + \ldots + \theta_{n-1} + \frac{\theta_2 - \theta_1}{9}$ = observed rise during the combustion, increased by the experimentally determined factor $\frac{\theta_2 - \theta_1}{9}$ (see foot-note).

v in the above equation may be $\pm$ according to whether the temperature of the calorimeter has an upward or downward tendency; v' is constantly negative.

An example of the method of taking the readings and applying the formula will serve to make the matter clear. The thermometer readings are given in fractions of the scale divisions:

A liquid of unknown composition was burned; weight taken, 0.5479 gram.

Observations.

Fore-period.		Combustion.		After-period.	
τ_1	118.15	θ_1	118.80 (ignition)	τ'_1	289.25
τ_2	118.30	θ_2	258.00	τ'_2	288.95
τ_3	118.45	θ_3	286.00	τ'_3	288.80
τ_4	118.60	θ_4	289.10	τ'_4	288.65
τ_5	118.70	θ_5	289.35	τ'_5	288.40
τ_6	118.80	θ_6	289.25	τ'_6	288.25
				τ'_7	288.05
$n_1 = 6$		$n = 6$		$n_2 = 7$	

From which we deduce the following :

$$\tau = \frac{\tau_1 + \tau_2 + \ldots + \tau_6}{6} = 118.50.$$

$$\tau' = \frac{\tau'_1 + \tau'_2 + \ldots + \tau'_7}{7} = 288.62.$$

$$v = \frac{\tau_6 - \tau_1}{5} = +0.13.$$

$$v' = \frac{\tau'_7 - \tau'_1}{6} = -0.20.$$

$$\sum_1^{n-1} \theta r = \theta_1 + \theta_2 + \ldots + \theta_{n-1} + \frac{\theta_2 - \theta_1}{9} = 1256.72.$$

$$\frac{\theta_1 + \theta_n}{2} = 204.02.$$

Whence follows :

$$\Sigma \Delta t = \frac{0.33}{170.12} (1256.72 + 204.02 - 711.00) - 0.65.$$

$$\Sigma \Delta t = +0.80.$$

This correction then added to the final temperature reading of the period of combustion, *viz.*, 289.25, gives as the corrected maximum $\theta_n = 290.05$. The temperature at the beginning of the combustion is $\theta_1 = 118.80$. Hence the rise in temperature during the combustion, expressed in degrees, is :

$$\theta_n - \theta_1 = 1^\circ.7125.$$

This increase is due not solely to the burning of the substance whose heat of combustion is to be determined, but a portion is caused by the burning of the cellulose film, the iron wire used as fuse, and the nitrogen in the bomb burned to

nitric acid. These, however, are factors which are either known or can be readily calculated, *e. g.*:

	Calories.
Heat given out, 1.7125 × 2900 (water value of the entire apparatus)	4966.25
To which is to be added for unburned carbon of the film,[1] 0.0035 gram × 8100.0 cal.	28.35
Total	4994.60

Heat due to:

	Calories.
Cellulose, 0.0147 gram × 4185.4	61.51
Iron wire, 0.0064 " × 1601.0	10.20
Nitric acid (by titration)	10.00
Total	81.71

$$4994.6 - 81.71 = 4912.89 \text{ cal.}$$

This amount of heat is produced by 0.5479 gram substance; hence the heat of combustion per gram is:

$$4912.89 \div 0.5479 = 8966.77 \text{ cal.}$$

If the composition and the molecular weight of the substance is known, the molecular heat of combustion and the heat of combustion at constant pressure can be easily calculated from that at constant volume. These are given for each substance studied.

For convenience of reference the observations, together with the deduced heat values, have been tabulated, using for the purpose the original symbols of the Regnault-Pfaundler-Stohmann correction formula with the significations ascribed to them on page 10.

In nearly every case determinations have been made with different samples of substance, and in each instance before and after recrystallization, redistillation, etc. This furnishes a severe test for the purity of the substance, since the heat values are very sensitive to impurities, more so than the usual chemical tests, which, however, were also made use of. In each instance the substance used was thoroughly dried by standing several days over solid caustic potash, and distilled immediately before using.

[1] In the tables which follow, this correction has been applied to and reported in the value given for the cellulose, thus simplifying the correction.

Table I.—Pyridine.[1] C_5H_5N. 79.06.

	Number of determination.[2] I.	II.	III.	IV.	V.	VI.
Amount of substance, gram.	0.5932	0.6264	0.9839	0.5909	0.5381	0.8537
v	0.09	0.10	0.10	0.29	0.20	0.21
v'	—0.23	—0.30	—0.66	—0.05	—0.09	—0.38
τ	49.63	55.80	213.90	62.19	32.70	34.42
τ'	221.29	235.91	505.90	236.12	192.41	315.21
$\sum_{1}^{n-1} \theta_r$	712.73	768.04	2399.40	1247.38	806.01	887.09
n	5	5	7	7	6	5
$\frac{\theta_n + \theta_1}{2}$	135.8	146.3	360.80	149.60	112.97	158.75
$\sum \Delta t$	0.76	1.01	2.69	0.14	0.31	1.00
θ_n (corr.), degrees	2.2251	2.3761	5.0896	2.3639	1.9316	2.8365
θ_1 "	0.4985	0.5600	2.1381	0.6295	0.3310	0.3485
$(\theta_n - \theta_1)$. 2911.6[3] cal.	5027.17	5287.76	8264.20	5029.76	4641.74	7215.20
Correction for Fe, cal.	10.2	10.2	9.1	10.3	10.3	10.3
" " HNO_3, cal.	13.5	16.0	10.6	14.0	12.5	19.0
" " cellulose, cal.	61.26	37.36	40.4	80.68	137.99	78.03

Heat Values.

No.	Per gram, cal.	Per gram-mol. Cal.	Per cent in terms of mean value = 100.
I.	8331.4	658.4	99.96
II.	8340.0	659.4	100.09
III.	8338.3	659.2	100.07
IV.	8334.4	658.9	100.02
V.	8327.4	658.4	99.93
VI.	8326.0	658.3	99.92
Mean,	8332.9	658.8 for constant volume 659.2 " " pressure	} at 15°

—16.7 heat of formation

[1] In the table all temperature values—unless otherwise stated—are expressed in fractional parts of the Beckmann scale divisions.
[2] Nos. V. and VI. were made with a specially purified sample received from Kahlbaum.
[3] In No. III. the water value was 2800, in Nos. IV., V., and VI. it was 2900.

Table II.—α-Picoline. C_6H_7N. 93.11.

	Number of determination.[1] I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Amt. of subst., gram.	0.6693	0.6328	0.6529	0.6273	0.6258	0.5872	0.6115	0.5969
v	0.23	0.20	0.26	0.19	0.20	0.21	0.15	0.23
v'	—0.21	—0.20	—0.21	—0.20	—0.18	—0.13	—0.19	—0.13
τ	122.05	118.62	112.36	124.37	106.30	98.61	150.23	93.12
τ'	314.34	310.31	310.36	316.60	298.73	279.27	337.01	276.05
$\sum_{1}^{n-1} \theta r$	1101.47	1053.08	1051.04	1393.74	1300.07	1210.96	1497.44	1191.59
n	5	5	5	6	6	6	6	6
$\frac{\theta_n + \theta_1}{2}$	223.72	214.97	211.97	221.03	203.00	189.28	244.08	185.08
$\Sigma\, \Delta t$	0.63	0.61	0.62	0.81	0.71	0.45	0.78	0.91
θ_n (corr.), degrees	3.2548	3.1141	3.1157	3.1791	2.9991	2.7995	3.3833	2.7731
θ "	1.2260	1.1915	1.1300	1.2495	1.0680	0.9905	1.5060	0.9375
$(\theta_n - \theta_1) \cdot 2911.6$[2] cal.	5907.05	5597.84	5781.56	5595.84	5580.88	5246.10	5444.17	5323.24
Correction for Fe.	10.2	10.2	10.2	10.2	10.2	10.2	10.2	10.2
" " HNO_3	16.0	15.0	15.5	15.0	13.5	14.5	12.0	14.0
" " cellulose	28.91	33.51	28.07	72.60	67.02	71.99	75.07	84.37

Heat Values.

No.	Per gram, cal.	Per gram-mol. Cal.	Per cent in terms of mean value = 100.
I.	8743.4	814.1	99.84
II.	8753.3	815.0	99.96
III.	8772.8	816.8	100.18
IV.	8764.6	816.1	100.08
V.	8773.0	816.9	100.18
VI.	8769.4	816.5	100.14
VII.	8744.0	814.2	99.85
VIII.	8736.3	813.5	99.76
Mean,	8757.1	815.4 for constant volume 816.1 " " pressure	at 15°

—10.6 heat of formation

[1] Nos. IV. to VIII. represent a second sample of the base.
[2] The water value in Nos. IV., VI., VII., and VIII. was taken at 2900, in No. V. at 2890.

Table III.—β-Picoline. C_6H_7N. 93.11.

	Number of determination.[1] I.	II.	III.	IV.	V.
Amt. of substance, gram.	0.5034	0.6449	0.6375	0.6295	0.5624
v	0.13	0.24	0.20	0.24	0.17
v'	—0.17	—0.13	—0.17	—0.20	—0.22
τ	85.63	89.58	89.75	90.30	159.40
τ'	238.07	284.70	283.18	280.59	330.72
$\sum_{1}^{n-1} \theta r$	1042.42	946.66	942.70	1219.26	1487.24
n	6	5	5	6	6
$\frac{\theta_n + \theta_1}{2}$	162.23	187.58	186.90	186.00	245.65
$\sum \Delta t$	0.71	0.34	0.47	0.79	0.92
θ_n (corr.), degrees	2.3921	2.8534	2.8407	2.8189	3.3222
θ_1 "	0.8595	0.9015	0.9020	0.9090	1.6000
$(\theta_n - \theta_1)$. 2911.6[2] cal.	4462.32	5683.15	5644.72	5560.86	4994.38
Correction for Fe, cal.	10.2	10.2	10.2	10.2	10.2
" " HNO_3, cal.	12.0	14.5	16.5	16.0	12.5
" "cellulose, cal.	50.75	34.58	46.99	44.06	66.34

Heat Values.

No.	Per gram, cal.	Per gram-mol. Cal.	Per cent in terms of mean value = 100.
I.	8719.4	811.9	99.94
II.	8720.5	812.0	99.95
III.	8738.9	813.7	100.17
IV.	8722.2	812.2	99.97
V.	8722.2	812.2	99.97
Mean,	8724.6	812.4 for constant volume 813.1 " " pressure	} at 15°
		—7.6 heat of formation	

[1] No. V. was made with a second sample of β-picoline.

[2] The water value used in No. V. was 2900.

Table IV.—γ-Picoline. C_6H_7N. 93.11.

	Number of determinations. I.	II.	III.
Amt. of substance, gram.	0.6495	0.6712	0.5675
v	0.24	0.33	0.24
v'	—0.15	—0.12	—0.12
τ	116.43	81.99	108.53
τ'	316.22	288.82	282.58
$\sum_{1}^{n-1} \theta r$	1070.73	1244.73	1244.49
n	5	6	6
$\frac{\theta_n + \theta_1}{2}$	216.92	186.05	195.95
$\sum \Delta t$	0.43	0.40	0.43
θ_n (corr.), degrees	3.1713	2.8955	2.8333
θ_1 "	1.1715	0.8295	1.0900
$(\theta_n - \theta_1)$, 2900 cal.	5799.42	5991.40	5055.57
Correction for Fe, cal.	10.2	10.2	10.2
" " HNO_3, cal.	14.5	17.0	14.5
" " cellulose, cal.	82.34	85.50	54.06

Heat Values.

No.	Per gram, cal.	Per gram-mol. Cal.	Per cent in terms of mean value = 100.
I.	8764.3	816.0	100.00
II.	8758.5	815.5	99.94
III.	8769.7	816.6	100.07
Mean,	8764.2	816.0 for constant volume 816.7 " " pressure } at 15°	
		—11.2 heat of formation	

Of the pyridine bases, so far as known to us, the heat of combustion of one only, pyridine, has been previously determined. This has been done by Thomsen,[1] using pyridine vapor, and by Delépine,[2] who determined it for the liquid. The former gives the value 675.1 Cal. for the vapor at 18° C., while Delépine gives 665.1 Cal. for the liquid, from which he calculated the value 673.7 Cal. for the vapor. The numbers obtained by us, *viz.*, 659.2 Cal. for the liquid and 667.6 Cal. for the vapor—the latter calculated from the former by addition of the molecular heat of evaporation (see p. 31)—are somewhat lower

[1] Thermochem. Untersuch, **4**, 144.
[2] Compt. rend., **126**, 1794 (1898).

than those given by these two observers. We feel inclined to consider our values as more nearly correct, great pains having been taken to have a pure product for the purpose of these experiments. They are, moreover, when considered in conjunction with the corresponding values obtained from the higher homologues, more nearly in accord with the previously observed rule for the increase in thermal value in an homologous series. On account of the lack of detailed information, especially as regards methods of purification, we find it impossible to criticise the results obtained by these investigators more nearly. The fact that commercial pyridine, unless very carefully purified, is almost sure to contain traces of higher homologues, suggests the possibility of the higher results being due to this cause.

An examination of the tabulated values shows that certain regularities exist for the pyridine bases which are closely in accord with those observed for other homologous series. It will be seen, for instance, upon considering the following table, that a constant ratio holds between pyridine and its higher homologues, *viz.* :

	Heat per gram-mol., Cal.	Difference from pyridine, Cal.
Pyridine, C_5H_5N	659.2	....
α-Picoline, C_6H_7N	816.1	156.9
β-Picoline, C_6H_7N	813.1	153.9
γ-Picoline, C_6H_7N	816.7	157.5
	Mean,	156.1

This constant is approximately 156 Cal. The same value has been found by other observers, notably by Stohmann and his pupils, who have established it as a general rule, based upon a large number of observations upon homologous compounds in both the fatty and aromatic series. The relation may be formulated thus:

$$X = -H + CH_2 + 156 \text{ Cal.}^1$$

Or, in words, the change in the heat of combustion due to the addition or subtraction of $CH_2 = \pm 156$ Cal.

[1] Stohmann: J. prakt. Chem., [2], **35**, 41 (1887).

The time at our disposal has not been sufficient for the preparation and examination of other of the higher homologues of the series, but we have obtained as the result of a single determination, made with a very small quantity of lutidine, the mercury salt of which was obtained as a by-product during the preparation of γ-picoline, the following heat values:

Per gram.	Per gram-mol.	
	Constant volume.	Constant pressure.
cal.	Cal.	Cal.
9037.2	967.9	968.9

This gives as the average difference from the picolines, due to CH_2, the value 154 Cal., thus indicating the constancy of the ratio for the entire pyridine series.

We hope later, by examining the higher homologues of this series, to be able to bring further evidence in support of this, but consider it possible to establish from the above a formula which permits an approximate calculation of the heats of combustion of the pyridine compounds from their empiric formula, thus:

$$C_nH_{2n-5}N = 659.2 \text{ Cal.} + (n-5)\ 156 \text{ Cal.}^1$$

In support of this we give the following calculated and observed values:

Substance.	Heats of combustion at constant pressure. Calculated.	Observed.
	Cal.	Cal.
Pyridine	659.2	659.2
Picoline	815.2	815.3 (average of the three picolines)
Lutidine	971.2	968.9

On comparing the heats of combustion of the picolines with that of the metameric compound, aniline, determined by Petit,[2] it will be observed that another rule which has been established for the fatty and aromatic series is also valid for the pyridine compounds, *viz.*, that isomers possess practically the same heats of combustion, whereas metamers have a higher value,[3] thus:

[1] For analogous formulæ for aliphatic hydrocarbons see Berthelot and Matignon: Compt. rend., **116**, 1333 (1893).

[2] *Ibid.*, **106**, 1089.

[3] Ostwald: Grundriss der allgemeinen Chemie.

Substance.	Heat per gram. cal.	Heat per gram-mol. Constant volume. Cal.	Constant pressure. Cal.
α-Picoline	8757.1	815.4	816.1
β- "	8724.6	812.4	813.1
γ- "	8764.2	816.0	816.7
Aniline	8794.0	817.8	818.5

For comparison may be cited the respective data for the isomeric cresols[1] and their metamer, anisol :[2]

Substance.	Per gram, cal.	Per gram-mol. Constant pressure. Cal.
o-Cresol	8176.0	883.0
m- "	8157.0	881.0
p- "	8175.0	882.9
Anisol	8345.0	901.3

The values just given serve to bring out more clearly another point to which we wish to call attention, *viz.*, that in the case of isomers the position of the substituting group seems to produce a greater effect upon the energy content in the case of the meta than with the ortho and para compounds, for in both of the cases cited the heats of combustion of the ortho and para compounds are practically identical, while that of the meta compound is slightly lower.

An examination of the published data with the idea of determining the general character of this led to no very satisfactory conclusion, the data not being sufficient for the purpose, while some of that given is old and possibly in need of revision. The indications are that, in general, the meta compounds exhibit a variation from the ortho and para, being sometimes higher, occasionally agreeing, but more often giving lower values.[3]

Heats of Formation.

These have been tabulated above in conjunction with the heats of combustion (p. 14), from which they were obtained by first calculating the heats of combustion of the composing elements, using for this purpose the values C = 94 Cal., H_2 = 69

[1] Stohmann, Rodatz, and Herzberg: J. prakt. Chem., [2], 34, 312.
[2] *Ibid.*, 35, 23.
[3] Stohmann: Ztschr. phys. Chem., 6, 334 ff; 10, 410 ff.

Cal.[1] (since the nitrogen contained in the substance is not burned, but liberated in the elementary state, it is not here taken into consideration), and then subtracting from the sum thus obtained the heat of combustion of the corresponding compound, which gives as difference the heat of formation of the latter.

It has been shown above that the increase in the heat of combustion in the pyridine series, for each CH_2, is equal to 156 Cal. This enables us to calculate for this series the heat of formation of the CH_2 group, *viz.*:

$$C + O_2 = CO_2 + 94 \text{ Cal.};$$
$$H_2 + O = H_2O + 69 \text{ Cal.}$$

Therefore,

$$C + H_2 + O_2 = CO_2 + H_2O + 163 \text{ Cal.}$$

for the elements, while

$$CH_2 + O_2 = CO_2 + H_2O + 156 \text{ Cal.}$$

for the compound, which gives:

$$C + H_2 = CH_2 + 7 \text{ Cal.},$$

the heat of formation of CH_2, and this furnishes a general formula for the calculation of the heats of formation of pyridine and its homologues, *viz.*:

$$C_nH_{2n-5}N = -51.7 \text{ Cal.} + n.7 \text{ Cal.}$$

Specific Heats.

In his classical work upon the specific heats in homologous series of liquid organic compounds,[2] Schiff was able to show, as the result of an extraordinarily painstaking series of experiments upon a very large number of compounds, that the variation of the specific heat of a substance with the temperature is expressed by a very simple formula, *viz.*, that of a straight line; and further, that for an homologous series this variation is of a uniform nature, the same expression serving for all the members of the series, or they can be represented by a small number of parallel straight lines.

This, as well as certain other generalities contained in that

[1] Stohmann: Ztschr. phys. Chem., 6, 334.
[2] Ann. Chem. (Liebig), 234, 300 (1886).

article, induced us to undertake an investigation of the specific heats of the compounds of the pyridine series with the idea of determining to what degree the relations established by that author are general in character, or at least to determine whether this regularity extends to this series.

As a preliminary to the discussion of our results, which can best be done after the results themselves have been given, we may state that they are not entirely in accord with the laws deduced by Schiff, although the divergence is of such a character that, considering the difficulty of establishing a generalization from a small number of observations, it is not improbable that the accordance is, nevertheless, of a fairly satisfactory character. In carrying out work of this nature, it is necessary, in order to attain a satisfactory degree of accuracy, to consider and eliminate as far as possible, the various conditions operating against the accuracy of the method. Schiff has already called attention to some of these,[1] the chief of which are the condition of purity of the material used and the possible error attached to the Berthelot form of apparatus, due to the immersion of the enclosed thermometer along with the container of the liquid during the cooling of the latter. Regarding the condition of purity of our substances, we have already spoken under the description of the methods of purification and the determination of the heats of combustion. The latter source of error was avoided by the use of the Schiff form of apparatus,[2] consisting of a platinum vessel made in the form of a cross, which acts admirably as a stirrer, and provided with a short, wide, thin-walled glass tube inserted tightly by means of a cork, which was also used as a handle in stirring. The thermometer was inserted loosely through this, by means of a cork, and dipped into the liquid below; before bringing the vessel into the calorimeter, the thermometer was removed and a small calcium chloride tube inserted to prevent the absorption of moisture. Any uncertainty caused by variation in the amount of heat given up by the thermometer was thus obviated.

In addition to the above-mentioned sources of error there

[1] *Loc. cit.*, 302.

[2] *Loc. cit.*, 303, with cut of apparatus.

are two others which should be considered, first, a part of the substance exists at the time of immersion into the calorimeter in the form of vapor, a portion of which, corresponding to the difference between the vapor pressures at the higher and the lower temperatures is condensed to liquid, so that there is included in the heat given off the heat of evaporation of this portion of the liquid, thus giving rise to too high a result. The second source of error is that due to the unknown loss of heat in transferring the platinum vessel from the heating apparatus to the calorimeter. This loss was reduced to a minimum by having the heating apparatus placed relatively near the calorimeter, the latter naturally being carefully shielded from radiated heat, and in such a position that the transfer could be made in the least possible time, never more than a fraction of a second being required. We have sought to reduce the first-mentioned source of error to a minimum by never heating the liquid more than to within 10° of its boiling-point. The two sources of error have a tendency to counteract each other, which lessens, to some degree, the absolute error of the method. The agreement in Schiff's results as well as in our own shows that the error thus introduced is of a negligible character.

The liquid, whose specific heat was to be determined, was heated by means of the vapors of a suitable liquid to the desired temperature. For heating liquids we used acetone, alcohol, water, toluene, and mixtures of toluene and xylene. The temperature of the liquid to be studied was taken by means of an immersed thermometer, being further controlled by surrounding the projecting stem with a wide glass tube whose upper end was closed by a cork and containing a second thermometer so placed that the medium temperature of the mercury thread outside the flask could be determined and the necessary correction made. The readings were taken by means of a cathetometer telescope and could be made with accuracy to hundredths of a degree. The immersion of the platinum flask into the water of the calorimeter did not take place until the liquid had shown a constant temperature for fifteen to twenty minutes.

As calorimeter thermometer we used an instrument constructed by the well-known instrument-maker, Golaz, in Paris; this was divided into 0°.02, and the readings were estimated to the thousandths by means of a strong lens. The thermometer calibration was controlled by comparison with a normal instrument, the comparison having been made a short time before using.

The calorimeter vessel was of such size that with 500 cc. water the platinum cross was immersed to just below the cork. The weight of the liquid taken was usually 40–50 grams, determined at the end of each experiment and corrected—as was that of the water in the calorimeter—for density, the corrected values being used in the calculations.

As unit of heat, we used the so-called *15° water-calorie*, defined as that quantity of heat required to raise the temperature of 1 gram water from 14°.5 to 15°.5, measured in terms of the hydrogen thermometer.[1] For purposes of calculation we have availed ourselves of the determinations made on the specific heat of water between 0° and 100° by Lüdin,[2] and have, for purposes of extrapolation, used the formula given by him, *viz.*:

$$C_{T,\theta} = 1 + \frac{\alpha}{2}(T + \theta) + \frac{\beta}{3}(T^2 + T\theta + \theta^2) + \frac{\gamma}{4}(T^3 + T^2\theta + T\theta^2 + \theta^3)\text{; where}$$

C = medium specific heat of water between the temperatures T° and θ°.

$$\frac{\alpha}{2} = -\ 0.000271396.$$

$$\frac{\beta}{3} = +\ 0.00000484567.$$

$$\frac{\gamma}{4} = -\ 0.000000021214.$$

The value thus obtained, divided by $C_{15} = 0.9949$,[3] gives the desired mean specific heat between T and θ.

[1] Warburg: Referat über die Wärmeeinheit, Leipzig (1900), p. 13; Kohlrausch, Lehrbuch der prakt. Physik., 9th ed. (1900), p. 179.

[2] Die Abhängigkeit der specif. Wärme des Wassers von der Temperatur—Mitteilung der naturwiss. Gesell. Winterthur, Heft II (1900); also Warburg: *Loc cit.*, p. 14.

[3] The true specific heat of water at 15°, $C_0 = 1$.

The thermometer readings were corrected by means of the Regnault-Pfaundler formula,[1] and the specific heat values calculated according to the following equation:

$$\Delta T[(G \times x) + (w \times s)] = \Delta\theta(W \times s'),$$

which gives, on solving for x,

$$x = \frac{\Delta\theta(W \times s') - w \times s}{G\Delta T}.$$

Here:

x = specific heat of the liquid between T° and θ°.
s = specific heat of water between T° and θ°.
s' = specific heat of water between 15° and θ°.
T = temperature of the liquid at the moment of immersion.
θ = (corr.) end temperature of the water (also of the liquid.
t = temperature of the water at the moment of immersion.
$\Delta T = T° - \theta° =$ (corr.) temperature change in the liquid.
$\Delta\theta = \theta° - t° =$ (corr.) temperature change in the water.
G = (corr.) weight in grams of liquid used.
w = water value of the platinum vessel.
W = total water value of the calorimeter (water + container + thermometer).

The symbols have the same significance in the tables on the next page.

An examination of the values given shows that between the same range of temperatures the specific heats of α- and β-picoline are practically identical and can be expressed by the equation

$$C_{T-\theta} = a + b\,(T + \theta)$$

for the mean specific heats, in which a has the value 0.3848 and b the value 0.000387, *i. e.*,

$$C_{T-\theta} = 0.3848 + 0.000387\,(T + \theta).$$

For the true specific heat the equation becomes

$$C_t = a + 2bt,$$

[1] Pogg. Ann., 129, 102.

Table V.—Pyridine.

No.	G.	W.	w.	s.	s'.	T.	θ.	t.	ΔT.	Δθ.	x.	Mean.
1	54.4068	517.953	2.7677	1.0061	0.9997	54.60	16.2611	14.4100	38.3389	1.8511	0.4083	0.4084
2	54.3862	"	"	"	"	54.65	16.4830	14.6400	38.1670	1.8430	0.4085	
3	54.4682	"	"	"	"	76.47	17.4332	14.5420	59.0368	2.8912	0.4144	0.41445
4	54.4342	"	"	"	"	76.47	17.9277	15.0620	58.5423	2.8657	0.4145	
5	50.3644	"	2.7686	"	"	98.22	20.6820	17.0900	77.5380	3.5920	0.4209	0.4201
6	50.3000	"	"	"	"	98.31	21.5440	17.9990	76.7660	3.5450	0.4193	
						α-Picoline.						
1	46.3457	517.953	2.7676	1.0061	0.9997	76.80	19.0593	16.5700	57.7407	2.4893	0.4216	0.42195
2	46.3259	"	"	"	"	76.81	19.2434	16.7590	57.5666	2.4844	0.4223	
3	46.4559	"	"	"	"	98.41	19.5505	16.0820	78.8595	3.4685	0.4303	0.4295
4	46.3893	"	"	"	"	98.32	20.0952	16.6700	78.2248	3.4252	0.4287	
5	46.1739	"	"	1.0066	"	108.71	18.8932	14.9280	89.8168	3.9652	0.4347	0.43465
6	46.1035	"	"	"	"	108.82	19.4389	15.5010	89.3811	3.9379	0.4346	
7	46.1973	"	"	"	"	118.10	21.8279	17.5400	96.2721	4.2879	0.4386	0.43895
8	46.1045	"	"	"	"	118.47	19.4806	15.0760	98.9892	4.4046	0.4393	
						β-Picoline.						
1	45.6799	517.953	2.7676	1.0061	0.9997	76.62	17.9893	15.4800	58.6307	2.5093	0.4242	0.4245
2	45.6608	"	"	"	"	76.67	18.3588	15.8620	58.3112	2.4968	0.4248	
3	45.6033	"	"	"	"	96.41	19.9750	16.6670	76.4350	3.3080	0.4303	0.4299
4	45.5827	"	"	"	"	96.88	19.8331	16.5060	77.0470	3.3271	0.4294	
5	45.9110	"	"	1.0066	"	121.83	19.7478	15.2560	102.0822	4.4918	0.4356	0.43565
6	45.8352	"	"	"	"	121.51	19.9381	15.4740	101.5719	4.4641	0.4357	
7	45.7522	"	"	"	"	129.71	20.5142	15.6800	109.1958	4.8342	0.4402	0.4414
8	45.7085	"	"	"	"	129.39	20.7720	15.9480	108.618	4.8240	0.4427	

or, substituting the values of a and b given above,

$$C_t = 0.3848 + 0.000774t.$$

For pyridine the equations are:

$$C_{T-\theta} = 0.3915 + 0.000242(T + \theta);$$

and

$$C_t = 0.3915 + 0.000484t.$$

A comparison of the values found with those calculated establishes the correctness of the above formulas, *viz.*:

Table VI.—Pyridine.

No.	T.	θ.	Specific heat. Found.	Specific heat. Calculated.
1	54.60	16.26	0.4083	0.4086
2	54.65	16.48	0.4085	0.4087
3	76.47	17.43	0.4144	0.4142
4	76.47	17.93	0.4145	0.4144
5	98.22	20.68	0.4209	0.4196
6	98.31	21.54	0.4193	0.4198
		α-Picoline.		
1	76.80	19.06	0.4216	0.4219
2	76.81	19.24	0.4223	0.4220
3	98.42	19.55	0.4302	0.4304
4	98.32	20.09	0.4287	0.4306
5	108.71	18.89	0.4347	0.4342
6	108.82	19.44	0.4346	0.4345
7	118.10	21.83	0.4386	0.4389
8	118.47	19.48	0.4393	0.4382
		β-Picoline.		
1	76.62	17.99	0.4242	0.4214
2	76.67	18.36	0.4248	0.4216
3	96.41	19.97	0.4303	0.4298
4	96.88	19.83	0.4294	0.4300
5	121.83	19.75	0.4356	0.4394
6	121.51	19.94	0.4357	0.4395
7	129.71	20.51	0.4402	0.4429
8	129.39	20.77	0.4427	0.4429

We were unable to establish for this series the correctness of Schiff's rule, that in homologous series the curves expressing the change of specific heat with the temperature are represented by a series of parallel straight lines (when not by

the same line). A glance at the temperature factor for pyridine and the picolines shows that for this series, as far as it applies to the two homologues considered, the lines are not parallel, but slightly divergent, as is shown by the following curves. In Table A are represented the mean specific heats as actually found, for the temperatures given, while in Table B are shown the specific heats calculated from the formulas given above and reckoned for the same ranges of temperature for pyridine and for the picolines. The temperatures used in the calculation were selected arbitrarily, but as far as possible with the idea of keeping closely within range of the temperature intervals used in the actual observations.

The specific heat of pyridine has been previously determined by Colson,[1] Delépine,[2] and by Kahlenberg.[3] None of these find a value entirely in accord with that obtained by us. Colson gives 0.412 between 34°.65 and 14°.07; Delépine gives 0.4241 between 98° and 16°, while Kahlenberg finds 0.4313 between 108° and 21°. It is difficult to estimate the relative value of these; Colson states that he did not aim at a very great exactitude; Delépine gives too little data to enable us to determine the actual conditions under which he operated. Kahlenberg's value appears to us to be too high, though as it is likely that his unit for the calorie was different from that used by us, we are unable, for lack of the necessary data, to make a comparison of the two values by recalculating his results. Since that author also made use of the Berthelot form of apparatus, the disadvantages of which Schiff has already called attention to,[4] it is not improbable that this may have influenced his results to some extent.

Kahlenberg has also determined the specific heat of α-picoline[5] as 0.4342 between 124° and 22°. This value, which is somewhat lower than ours, may also be found more nearly in accord with it upon recalculating to the same units.

It is evident that, in general, in the determination of the

[1] Ann. chim. phys., [6], **19**, 409 (1890).
[2] Compt. rend., **126**, 1794 (1898).
[3] J. Phys. Chem., **5**, 229 (1901).
Ann. Chem. (Liebig), **234**, 304.
[4] *Loc. cit.*, p. 284.

specific heats of liquids, too little attention has heretofore been paid to the proper purification of the substances used. Schiff has called attention to this,[1] and our experience fully supports his statement that the slightest trace of impurity produces a very marked influence upon the specific heat.

Heats of Evaporation.

For the purpose of determining the latent heats of evaporation of the substances under investigation, we made use of the apparatus of Schiff,[2] constructed entirely of platinum. Kahlenberg, in an article bearing upon this subject,[3] raises an objection to this form of apparatus, stating that in the case of liquids with high boiling-points the liquid condenses in the trap and eventually some of it runs over into the condenser. Our results do not bear out this objection, for, although working with moderately high-boiling liquids, we failed to note a single instance in which this happened. It is probable that Kahlenberg's tests were made with a glass trap, which, on account of the relatively high specific heat of glass, might require a considerable amount of liquid to be condensed in the trap before the inner tube assumed the temperature of the vapor, especially so if the tube leading from the boiling vessel to the trap was not sufficiently wide or the heating too rapid to permit the condensed liquid to run back into the retort. With a wide tube of metal, such as silver or platinum, and a proper regulation of the rate of boiling, this would not be the case, as the results given by Schiff who used a silver tube, and those to be presented by us, when a tube of platinum was used, most definitely prove. An entire apparatus of metal naturally possesses another advantage in that it gives up its heat much more readily than one of glass, and can be used for all forms of liquids, some of which attack glass.

The operation was carried out under conditions similar to those described under specific heats, using a similar form of calorimeter and thermometer. The calorimeter vessel was of such size that the condenser was immersed to a point just be-

[1] *Loc. cit.*, p. 307.
[2] Ann. Chem. (Liebig), **234**, 338 (1886).
[3] J. Phys. Chem., **5**, 217 (1901).

neath the cork, and the water and thermometer were carefully protected from influences of radiation, which can be more conveniently done with this form of apparatus than with the upright heater of Berthelot or that described by Kahlenberg.[1]

The apparatus was thoroughly tested by using liquids whose latent heats of evaporation are known. In every case from 20 to 30 grams of substance were condensed, which required four to six minutes, the boiling being so regulated that the thermometer rose only about one degree per minute, the total rise in the calorimeter being usually 4° to 5°. The 15°-calorie was used as the unit in making the calculations, and all weighings were corrected for the specific gravity of the liquid.

The latent heats of vaporization of pyridine and of α-picoline have already been determined by Kahlenberg.[2] Our results upon the specific heats of these liquids, however, differing so markedly from his, and furthermore, as has been shown above, the specific heat varying with the temperature, it was thought best to repeat his determinations of the heats of evaporation of these substances, using the extrapolated values for the specific heats at the boiling-point of the liquid in question, making use of the equation given on page 24 for this purpose. From this the mean specific heat between the boiling-point and the end temperature could be obtained and inserted in the calculations.

The formula used was

$$H = \frac{W(\Delta\theta \times s) - G(\Delta T \times \delta)}{G},$$

in which, and for the following tables:

B_o = barometric reading, reduced to 0°.
T = boiling-point of the liquid.
G = weight of liquid condensed.
W = total water value of the apparatus (water + water value of the solid parts).
s = specific heat of water between 15° and θ°.
δ = specific heat of the liquid between T° and θ°.

[1] *Loc. cit.*, p. 221.
[2] *Loc. cit.*

θ = end temperature in the calorimeter.
t = original temperature of the water.
$\Delta T = T° - \theta° =$ (corr.) temperature change in the liquid.
$\Delta\theta = \theta° - t° =$ (corr.) temperature change in the water.
H = latent heat of evaporation per gram substance, expressed in 15°-calories.

From the data contained in the table the values found for the Trouton constant,[1] $\frac{MH}{T} = C$, are: For pyridine, 21.9; α-picoline, 21.5; β-picoline, 21.3, the mean of which is 21.6. This value approaches closely to that found by Schiff for a large number of the esters of the fatty series and also certain of the aromatic hydrocarbons. Schiff's number is 20.8.[2] It appears evident, therefore, that in the pyridine series also, the molecular heats are proportional to the absolute temperatures at which evaporation takes place.

In order to obtain the normal heats of evaporation, *viz.*, those which correspond to the boiling-points under normal pressure—this constituting in reality the only condition under which a true comparison of these can be made—we have, using the mean 21.6, deduced these to be:

	Calories.
Pyridine	106.1
α-Picoline	93.3
β- "	96.7

Kahlenberg's value for pyridine, 104.0,[3] recalculated to normal conditions, yields as the normal heat of evaporation 104.3. His number for α-picoline, 90.75,[4] gives in the same way as the normal heat of evaporation, 90.9. Considering the differences in method, and more particularly in the specific heats used, this must be pronounced a fairly satisfactory agreement.

It was further of interest to calculate for these substances the constant expressing the molecular rise of boiling-point, especially since pyridine, and possibly also α-picoline, seem well suited as solvents for molecular weight determinations.

[1] Phil. Mag., [5], 18, 54 (1884); Beiblätter, 8, 643.
[2] Ann. Chem. (Liebig), 234, 348 (1886); Ostwald: Lehrbuch der allgemeinen Chemie, 2te Aufl., 1, 354.
[3] *Loc. cit.*, p. 230.
[4] *Loc. cit.*, p. 286.

Table VII.

No.	Substance.	B. mm.	T.	G.	W.	s.	δ.	θ.	t.	ΔT.	Δθ.	H.	Mean.
1	Pyridine	715.9	113.55	29.0457	980.06	0.9997	0.4238	20.0528	15.700	93.4972	4.3528	107.2	
2	"	720.2	113.71	29.1172	"	"	0.4234	19.5785	15.206	94.1315	4.3725	107.3	107.33
3	"	719.1	113.67	30.9310	"	"	0.4238	19.9310	15.280	93.7390	4.6510	107.6	
4	α-Picoline	727.8	127.73	30.8353	"	"	0.4417	19.3363	14.9140	108.3937	4.4223	92.65	
5	"	727.8	127.73	26.2262	"	"	0.4415	18.7726	15.0020	108.9574	3.7706	92.76	92.7
6	β- "	723.3	141.73	24.1747	"	"	0.4473	19.7723	16.1040	121.9577	3.6683	94.12	
7	"	720.9	141.64	21.2152	"	"	0.4471	19.4047	16.1680	122.2353	3.2367	95.52	94.82

The calculation was made by inserting the normal heats of evaporation in the Arrhenius-Beckmann formula, $K = \frac{0.02T.^1}{H}$

The numbers found for K are:

Pyridine, K = 28.4;
α-Picoline, K = 34.6;
β- " K = 35.8.

From the values obtained by him, Kahlenberg calculated the boiling-point constant, K, for pyridine 28.8, and for α-picoline 35.6. Werner obtained by direct observation of the increase in the boiling-point, using pyridine as a solvent, K for pyridine = 30.07. The latter made no particular point, however, of using absolutely pure substance or of attaining great accuracy in the results.

Heats of Neutralization.

Although it is generally known that the heats of neutralization do not serve as an absolute measure of the affinities of acids or bases, we nevertheless undertook to determine the respective data for pyridine and for two of the picolines in order to ascertain whether the comparative values thus obtained follow the same order as their affinity-constants determined by us electrolytically.

For this purpose we availed ourselves of the excellent and simple form of apparatus described by Thomsen,[1] with the single modification that the upper vessel was of glass. This, however, was carefully protected from heat radiation, being surrounded with a thick layer of felt with an air space between the two, and further, by a polished metal cylinder covered with a plate of hard rubber, which did not touch the inside vessel. The temperature of the room during the whole investigation was kept between 17° and 18° C.[2] The thermometers used were of the type described under specific heats and had previously been compared with each other throughout their entire ranges of temperature.

The observed differences in temperature between the acid

[1] Thermochem. Untersuch., 1, 19.
[2] Thomsen: *Loc. cit.*, p. 59.

and alkali before mixing were very slight, amounting to only a few tenths of a degree.

For the neutralization equal quantities (300 cc.) of exactly N/2 hydrochloric acid and N/2 solution of the base were used, the solutions being made in specially prepared "conductivity" water, freed as far as possible from carbon dioxide and ammonia. The solution of the base was prepared by weight, using the thoroughly dried and recently distilled base, the weighings being made in a specially constructed vessel which closed perfectly and from which, without exposure to the air, the liquid could be run directly into water contained in an accurately calibrated measuring-flask. All volumes were taken at 17°.5 C.

In order to determine the amount of acid actually consumed and likewise of base neutralized, the acid container—the upper vessel—was rinsed out at the end of the experiment and the unused acid titrated with N/10 barium hydroxide solution. The amount thus obtained was deducted from the total taken (300 cc.) and the corrected value introduced in the final calculation.

The time required, after mixing, to attain the maximum was never more than one minute. The calculations were made by means of Berthelot's formula,[1] assuming the weights and specific heats of the liquids to be the same as those of water. This is not absolutely the case, but as both Thomsen[2] and Berthelot[3] have proved, the error thus introduced is negligible in character.

In the tables which follow, the symbols used have the following significance:

t_a = (corr.) temperature of the acid before mixing.
t_b = (corr.) temperature of the base before mixing.
W_1 = (corr.) water value of the acid.
W_2 = water value of the base + the solid parts in terms of water.
θ^4 = (corr.) mean temperature of the acid and base at time of mixing.

[1] Traité practique de Calorimétrie Chimique, p. 72 ff.
[2] *Loc. cit.*, 1, 52.
[3] *Loc. cit.*, p. 76.
[4] All temperatures are expressed in degress.

T = (corr.) maximum temperature of the mixture.
$\Delta\theta$ = rise in temperature.
Q = amount of heat given out, expressed in calories.
H = molecular heat of neutralization in calories.

For purposes of comparison with the numbers thus found, we have only the determinations made on pyridine by Colsen[1] and by Berthelot.[2] The former found for the heat of neutralization of pyridine (1 molecule in 2 liters) with hydrochloric acid (1 molecule in 1 liter), 5.2 Cal., while the latter obtained, using pyridine (1 molecule in 2 liters) and hydrochloric acid (1 molecule in 2 liters) at 22°, 5.1 Cal. The agreement between these investigators, using the same form of apparatus, is indeed very close, while the lower value obtained by us, 4.8 cal. seems not entirely comparable with that found by them. We are, nevertheless, inclined to insist upon the correctness of our number as expressing the true heat of neutralization of this substance. The fact that Colson and Berthelot, working at widely different temperatures, the latter at 22°, the former—who does not give the temperature of the surroundings—presumably, however (from the data given), about 13.°5–14°, obtained nearly the same value, leads to the conclusion that for pyridine hydrochloride the temperature influence is very small.[3] We may be allowed to surmise, therefore, that the discrepancy between their results and ours may be due to a difference in the character and purity of the bases used.[4]

From the results given in the table above it appears that both picolines have a higher heat of neutralization than pyridine, α-picoline giving a somewhat higher value than the β-compound. As will be shown below, the affinity-constants for the three substances follow the same order.

ELECTROCHEMISTRY OF THE PYRIDINE BASES.

The affinity constants for pyridine and α-picoline—also for s-collidine—have been determined by Goldschmidt and Salcher[5]

[1] Ann. chim. phys., [6], **19**, 411 (1890).
[2] *Ibid.*, **21**, 381.
[3] cf. Thomsen: *Loc. cit.*, p. 60.
[4] See, also, Kahlenberg, *Loc. cit.*, p. 267.
[5] Ztschr. phys. Chem., **29**, 89 (1899).

Table VIII.

No.	Substance.	t_α.	t_β.	W_1.	W_2.	θ.	T.	$\Delta\theta$.	Q.	H.	Mean.
1	Pyridine	17.767	17.358	298.50	307.1	17.558	18.735	1.177	713.42	4780.0	4776.2
2	"	17.868	17.606	298.92	"	17.735	18.914	1.180	715.09	4772.4	
3	α-Picoline	17.381	17.227	298.57	"	17.303	18.779	1.476	893.98	5988.5	5979.6
4	"	17.614	17.365	298.71	"	17.488	18.960	1.472	891.75	5970.7	
5	β- "	17.902	17.621	298.57	"	17.759	19.161	1.402	849.2	5688.4	5689.8
6	"	18.167	17.718	298.68	"	17.935	19.338	1.403	849.9	5691.1	

through a study of the aminolysis of these with aniline, using various acids; also, for pyridine, by measuring the hydrolytic dissociation of the nitrate.

Having at hand a supply of the very pure material used for the thermochemical investigations on these bases, and desiring to compare the three picolines as to their relative affinities, we have made measurements of the electrolytic conductivities of salts of these with this end in view.

Direct measurements of the conductivities of the bases themselves as a means of determining the affinities, did not promise to be successful, these being too small to give reliable values. Goldschmidt and Salcher attempted this with α-picoline, the most pronounced base of the series, without, however, obtaining very satisfactory results. It was, therefore, decided to make use of the hydrolytic method of Walker,[1] with application of the Arrhenius modification of the Guldberg-Waage law.[2]

For this purpose we sought to obtain a salt which could be prepared in a state of purity and which was sufficiently stable to allow the making up of solutions of definite concentration by weight. With the exception of pyridine—which forms a stable nitrate—none of these bases yield salts with the commoner acids ordinarily used in such measurements which are either sufficiently stable or sufficiently non-hygroscopic to be conveniently used for the above purpose. It is possible indeed to prepare, as Bredig has done in his measurements of the ionic conductivities of the bases, salts of these by neutralization in solution. It is very difficult, however, to do this in the case of those bases whose salts are hydrolytically dissociated, since these have an acid reaction towards indicators, even when equivalent amounts of acid and base are present. The preparation of neutral salts by weighing, when the substances are volatile, is likewise a difficult task.

The only one of the well-conducting acids which appears to form salts with these bases capable of being purified by recrystallization, and of being weighed out in exact quantities seems to be picric acid. This forms beautiful, well-crystal-

[1] Ztschr. phys. Chem., 4, 319.
[2] *Ibid.*, 8, 17.

lized compounds with pyridine and the picolines, and is itself almost completely dissociated at moderate dilutions.[1]

The picrates, therefore, seemed suited to the measurements of the hydrolytic and electrolytic dissociations of the salts of these bases; they possess, however, the very decided objection that they are all quite difficultly soluble, and it was, therefore, necessary to make use of solutions at such dilutions that the measurements become somewhat uncertain, owing to the influence of the water, etc. We found it impossible to prepare solutions stronger than 1 molecule in 128 liters, but as the measurements made with these agreed well and gave fairly satisfactory results in most cases up to 1 molecule in 1024 liters, we have used these for the calculation of the affinity-constants.

For the purpose of preparing the salts, the picric acid was first purified by recrystallization from water and finally by conversion into the sodium salt according to the method given by Lea.[2] The acid, as finally obtained, was tested as to its melting-point, 122°.5, and its conductivity (see below). The salts were prepared in each case by making a concentrated solution of the acid, either in water or alcohol, and adding slightly more than the calculated amount of base, whereupon the picrates were immediately precipitated, the crystal mass filling the vessel. This was drained off by the aid of the pump, and the salt recrystallized, the pyridine and α-picoline picrates from water, the β- and γ-picoline picrates from alcohol. All yield difficultly soluble and well crystallized salts except the γ-compound, which crystallizes less well, and was more difficult to obtain pure, the best results being obtained by adding an excess of base and recrystallizing from strong alcohol. This behavior of the γ-salt is similar to that mentioned under the mercuric chloride salt (page 6), and the explanation there given can be applied to this as well. The melting-points obtained for the salts were: Pyridine picrate, 165°.5; α-picoline picrate, 164°; β-picoline picrate, 149°.5; and γ-picoline picrate, 161°–162°—the latter differing some-

[1] Ostwald: Ztschr. phys. Chem., 1, 77 (1887); Bader: *Ibid.*, 6, 289 (1890).
[2] Jsb., 1861, p. 635.

what from the melting-point given by Ladenburg, 167°.[1]

The water used in the measurements had a conductivity ranging between $0.9 \times 10.^{-6}$ and $1.5 \times 10.^{-6}$, and was obtained by a process of triple distillation through a battery of large retorts of Jena glass, so arranged that the neck of each served as a reflux condenser. The last retort was attached directly to a tin condenser; the entire apparatus was so connected that the distillate passed from one vessel into the other without coming in contact with the outer air. The distillation took place first from lime and permanganate, then from phosphoric acid, and finally from a nearly saturated solution of barium hydroxide. Before beginning the distillation, both ends of the apparatus were attached to a series of soda-lime tubes, and the air in the apparatus displaced by drawing through it a slow current of air freed from carbon dioxide. The supply water was introduced without opening the apparatus by means of a separatory funnel, the final distillate being siphoned off as needed. The supply water used had been previously distilled from a large tin still used only for such purposes. This water itself had a conductivity rarely exceeding $2 \times 10.^{-6}$. In all the conductivity measurements on the salts, the correction for water was brought into account as recommended by Ostwald.[2]

The conductivities were all determined at 25° C., the temperature being kept as exactly as possible at this point. The measurements are expressed in reciprocal Siemens units. An Arrhenius cell was used, the resistance capacity of which was determined after each series of measurements, using for this purpose a N/50 solution of potassium chloride.[3]

To test the method, measurements were first made upon the conductivities of pyridine and α-picoline picrates. Bredig, in his work upon the stoichiometry of the ions,[4] has determined the velocities of the pyridine and α-picoline ions, using the hydrochlorides for this purpose, while Goldschmidt and Salcher[5] have determined it for the pyridine ion, using the ni-

[1] Ann. Chem. (Liebig), **247**, 5.
[2] "Hand und Hilfsbuch", 2te Auf., p. 423.
[3] Ostwald: "Hand und Hilfsbuch", 1ste Auf., p. 273.
[4] Ztschr. phys. Chem., **13**, 191 ff. (1894).
[5] *Loc. cit.*

trate. We, therefore, had in these determinations an opportunity of testing the suitability of picric acid for such purposes, since, so far as known, it has not previously been so made use of.

Ostwald[1] and Bader[2] have both measured the molecular conductivity of picric acid, and the former that of sodium picrate. The two determinations made on the acid do not agree and, it furthermore appears probable that the velocity ascribed by Ostwald to the picric ion, 31.5,[3] is too high by several units. We, therefore, decided to redetermine the velocity of this ion, and used for this purpose the purified picric acid mentioned above, as well as the sodium salt, which was several times recrystallized from alcohol, its conductivity measured, and after a further recrystallization a second measurement made; the two agreed perfectly. Each set of measurements was made in duplicate.

Table IX.

Picric Acid, $C_6H_2(OH)(NO_2)_3 = 1:2:4:6$.

$\mu_\infty = 356$.

v.	μ_1.	μ_2.	Mean. μ.
32	316.9	316.8	316.9
64	328.5	328.8	328.7
128	337.3	337.2	337.3
256	344.3	344.6	344.5
512	351.1	350.8	350.9
1024	357.7	357.5	357.6

Table X.

Sodium Picrate, $C_6H_2(NO_2)_3ONa$.

μ_∞[4] $= 74.1$.

v.	μ_1.[5]	μ_3.	μ_3.	μ_4.	μ_a.	Mean. μ.
32	62.1	62.2	62.3	62.2	62.2	62.1
64	64.2	64.0	64.2	64.2	64.2	64.1
128	65.7	65.7	66.0	66.0	65.9	65.7
256	67.2	67.4	67.8	67.6	67.5	67.2
512	69.0	69.8	69.4	69.5	69.4	68.8
1024	71.3	71.9	71.7	71.8	71.8	70.5

[1] *Loc. cit.*

[2] *Loc. cit.*

[3] Ostwald: Lehrbuch, 2, 678.

[4] Calculated by use of Bredig's rule, Ztschr. phys. Chem., 13, 198.

[5] μ_1 and μ_2 were obtained with the same solution; μ_3 and μ_4 after further recrystallization; μ_a is the mean of all observations, and μ the corrected mean after deducting the conductivity of the water.

The values of μ_v for the acid are more nearly in accord with Bader's than with Ostwald's numbers, while for the salt, μ_v, for each concentration used, falls about 6 units below the value found at the corresponding dilution by Ostwald.

To calculate the velocity of the picric ion, we used the Kohlrausch law of the independent wandering of the ion,[1] expressed by the equation $\mu_\infty = a' + a'$, where a' is the velocity of the cation and a' that of the anion at infinite dilution. To obtain from this the value of a' we have only to transform the equation to $a' = \mu_\infty - a'$; since both μ_∞ and a' are known, the value of a' is also known.

The values of a'_H and a'_{Na} used were obtained from those given by Kohlrausch, expressed in reciprocal ohms and at 18°, *viz.*, $a'_H = 318$ and $a'_{Na} = 43.55$.[2] Our measurements having been made at 25° and in reciprocal Siemens units, the Kohlrausch values must be reduced to these conditions. For this purpose the temperature-coefficients α and β given by Kohlrausch were made use of and substituted in the temperature formula of Déguisne.[3]

$$K_t = K_{18}[1 + \alpha(t-18) + \beta(t-18)^2].$$

The value thus found, reduced to Siemens units by division by 1.066,[4] gives the desired number at 25°. The numbers thus found are $a'_H = 330$;[5] $a'_{Na} = 48.1$. Using the value a'_{Na} thus found, we obtain as the value for $a'_{Pic.} = \mu_\infty - a'_{Na}$, the number 26.0.

In order to determine the conductivities, and also the hydrolysis, of the salts under consideration, three solutions of each were prepared by weighing off the calculated amount of the salt. One portion was dissolved in water, a second portion in a N/32 solution of the corresponding base, and the third portion in a N/64 solution of the same.[6] Duplicate measurements were made with each solution, the mean of

[1] Wied. Ann., **6**, 1; **26**, 213. Ostwald: Lehrbuch, **2**, 639. Bredig: Ztschr. phys. Chem., **13**, 194. 225.

[2] Sitzungsber: Kgl. preuss. Akad. Wiss., Berlin, 1901, p. 1031; 1902, p. 581.

[3] "Die Temperatur-coefficienten des Leitvermögens sehr verdünnter wässeriger. Lösungen." Dissertation, Strassburg, 1895.

[4] Kohlrausch, Holborn, and Diesselhorst: Wied. Ann., **64**, 417 (1898).

[5] Compare Ostwald-Luther: "Hand und Hilfsbuch", p. 415.

[6] Bredig: Ztschr. phys. Chem., **13**, 214.

each series being here given under the respective headings μ_v (H_2O), $\overset{32}{\mu}_v$, and $\overset{64}{\mu}_v$ (for the solutions in N/32 and N/64 solution of base). In series μ_v pure water was used in making the dilutions. In the series $\overset{32}{\mu}_v$ and $\overset{64}{\mu}_v$ the dilutions were made with N/32 and N/64 solutions of the base respectively.

By this method—the conductivity of the base itself being so small as to be negligible, as compared with that of the salt—the hydrolysis was practically annulled and the necessary conditions to the equation $M_v = \mu_v$[1] fulfilled. As may be seen from the tables, the values of $\overset{32}{\mu}_v$ and $\overset{64}{\mu}_v$ are nearly identical, and we can therefore assume the mean of the two, μ_v, as the true electrolytic conductivity.

In order to save space, the values $100x$ and $\frac{K_3}{K_4}$, which are to be considered later, are inserted in the same tables.

Table XI.

Pyridine Picrate, $C_6H_2(NO_2)_3O.HNC_5H_5$.

$\mu_\infty = 72.4$.

v.[2]	M_v.	$\overset{32}{\mu}_v$.	$\overset{64}{\mu}_v$.	Mean. μ_v.	$100x$.	$\frac{K_3}{K_4}$
128	70.58	64.51	63.66	64.09	2.38	221×10^3
256	74.95	66.29	66.35	66.32	3.10	258×10^3
512	80.01	68.48	67.94	68.21	4.17	282×10^3

Mean, 253×10^3

Affinity-constant, $253\times10^3 \times 1.2\times10^{-14} = 3.0\times10^{-9}$

Table XII.

α-Picoline Picrate, $C_6H_2(NO_2)_3O.HNC_6H_7$.

$\mu_\infty = 66.8$.

v.	M_v.	$\overset{32}{\mu}_v$.	$\overset{64}{\mu}_v$.	Mean. μ_v.	$100x$.	$\frac{K_3}{K_4}$
128	60.71	58.34	58.41	58.38	0.84	1819×10^3
256	63.64	60.68	60.64	60.66	1.05	2297×10^3
512	66.61	63.51	63.15	63.33	1.14	3892×10^3

Mean, 2669×10^3

Affinity-constant, $2669\times10^3 \times 1.2\times10^{-14} = 3.2\times10^{-8}$

[1] See Bredig: *Loc. cit.*

[2] The values at v 1024 are omitted, as the agreement at this dilution was not very satisfactory.

Table XIII.

β-Picoline Picrate.

$\mu_\infty = 68.4.$

$v.$	$M_v.$	$\mu_v.$ (32)	$\mu_v.$ (64)	Mean. $\mu_v.$	$100x.$	$\frac{K_2}{K_1}.$
128	63.64	59.83	59.93	59.88	1.35	687×10^3
256	67.20	62.29	62.16	62.23	1.76	811×10^3
512	70.97	65.24	64.61	64.93	2.10	1131×10^3

Mean, 876×10^3

Affinity-constant, $876\times10^3 \times 1.2\times10^{-14} = 1.1\times10^{-8}$

Table XIV.

γ-Picoline Picrate.

$\mu_\infty = 66.3.$

$v.$	$M_v.$	$\mu_v.$ (32)[1]	$\mu_v.$	$100x.$	$\frac{K_2}{K_1}.$
128	62.43	57.99	57.99	1.59	498×10^3
256	65.29	60.22	60.22	1.78	791×10^3
512	68.30	62.75	62.73	1.87	1440×10^3

Mean, 909×10^3

Affinity-constant, $909\times10^3 \times 1.2\times10^{-14} = 1.1\times10^{-8}$

Using the value for the picric ion given above, and substituting this in the equation $\mu_\infty = a' + a'$, we obtain the following numbers expressing the velocities of the respective cations:

		Bredig.[2]	Goldschmidt and Salcher.[3]
Pyridine	a' 46.4	44.1	44.4
α-Picoline	a' 40.8	39.1	
β- "	a' 42.8		
γ- "	a' 40.3		

Although our numbers fall somewhat higher than those obtained by Bredig and by Goldschmidt and Salcher, considering the fact that we have used in our calculations Kohlrausch's most recent values expressing the velocities of the ions at in-

[1] The amount of material at our disposal was not sufficient to make the measurements in the N/64 solution of the base.

[2] *Loc. cit.* p. 231.

[3] Calculated from the data given by Goldschmidt and Salcher: *Loc. cit.*

finite dilution—those values differing somewhat from the ones used by the authors mentioned—the agreement must be regarded as of a satisfactory nature.

If we add to the numbers given above the value for the OH ion at infinite dilution, we obtain the values expressing the conductivities of the respective bases. Using Kohlrausch's value for $a'_{OH} = 174$, and calculating this to 25° and in Siemens units according to the method already described, we obtain 183.7. The bases, therefore, have the conductivities at infinite dilution expressed by the following numbers:

Pyridine hydrate, C_5H_5NHOH	230.1
α-Picoline hydrate, C_6H_7NHOH	224.5
β-Picoline hydrate, C_6H_7NHOH	226.5
γ-Picoline hydrate, C_6H_7NHOH	224.0

On comparing the velocities of the cations as given above, it will be evident that also for the cations of the pyridine series, the general rule suggested by Ostwald, and further developed by Bredig,[1] *viz.*, that "isomeric ions have the same velocities of transport," holds good, for the three picolines have approximately the same values. Attention may be called to the fact that the β-compound has a value differing slightly from the others, a condition which is also exhibited by the ion of meta compounds in general (see Bredig's table). This is in accord with the variation in the heats of combustion to which attention has previously been called. Bredig has also shown that the law of like velocities of transport does not hold good for the metamers (Cf. aniline, $a' = 38^2$).

For a determination of the relative affinities of the bases, the velocity method, which depends upon the rate at which saponification of an ester such as methyl acetate takes place, seemed excluded because the bases in question were not weak enough to admit of the application of the law of mass action, being considerably stronger than aniline.[3]

The measurement of the extent of hydrolysis of the salts, as determined electrolytically, promised to give somewhat

[1] *Loc. cit.*, 247 ff.

[2] To make the values comparable, the speed of aniline, 35.9, given by Bredig has been raised about 2 units.

[3] Walker: Ztschr. phys. Chem., 4, 327 (1889).

more satisfactory results, although even here it was not to be expected that the constants expressing the ratios between the dissociation of the base and that of water would be found of a completely satisfactory character, since the hydrolysis is too slight to give a sufficient difference between the conductivities of the non-hydrolyzed salt and that in which hydrolysis had taken place. Slight errors of observation under these conditions affect enormously the end result.[1] By working at higher temperatures, thus increasing the extent of the hydrolysis, this might have been obviated in part. Unfortunately, the time at our disposal did not permit of this being done.

Under these conditions the results as given cannot be considered as sufficiently accurate to indicate the absolute affinities, but suffice to give a qualitative measure of these, and to furnish a comparison between the affinities of these bases themselves.

The method used was that given by Walker[2] and containing the Arrhenius modification of the Guldberg-Waage law,[3] as expressed by the equation :

$$\frac{K_3}{K_4} = \frac{v(1-x)}{x^2},$$

where

v = the volume in liters containing 1 gram-molecule of the salt.

x = the degree of dissociation of the salt, assuming the amount originally present as 1.

K_3 = the dissociation or affinity-constant of the base.

K_4 = the dissociation-constant of water.

The value of x can be determined by means of the conductivity of the hydrolytically dissociated salt, using the method suggested by Bredig,[4] in which, in order to obtain the true electrolytic conductivity (that in which no hydrolysis is present), a solution of the weak base is used as solvent and for dilution purposes. Expressing the conductivity of the

[1] Bredig: *Loc. cit.*, 324, 325.

[2] *Loc. cit.*, p. 333.

[3] Ztschr. phys. Chem., **8**, 17; see also Bredig: *Ibid.*, **13**, 321.

[4] *Loc. cit.*, p. 213.

hydrolytically dissociated salt by M_v, that of the electrolytically dissociated salt by μ_v, and that of the acid by μ_A, the value of x can be determined from the formula

$$M_v = (1-x)\mu_v + x\mu_A,$$

or

$$x = \frac{M_v - \mu_v}{\mu_A - \mu_v}.$$

Substituting, in this expression, the values found for the picrates as given in the table under M_v and μ_v, and the value μ_A of picric acid for the corresponding dilution, we obtain the values of x for each dilution and from these that of $\frac{K_3}{K_4}$ = constant.

As has been remarked, the values of $\frac{K_3}{K_4}$ found are not exactly constant, and for the reasons already stated. They serve, however, to give an approximate value from which that of K_3, the affinity-constant can be obtained by multiplication by 1.2×10^{-14} expressing the dissociation-constant K_4 of water.[1] The affinity-constants thus obtained, *viz.*,

Pyridine	$3.0.10^{-9}$
α-Picoline	$3.2.10^{-8}$
β-Picoline	$1.1.10^{-8}$
γ-Picoline	$1.1.10^{-8}$

are, in all probability, somewhat too high. That of γ-picoline undoubtedly is, for other considerations—notably, the behavior of salts of the two bases—indicate that it is somewhat weaker than the β-compound.[2] For the others, the affinities follow in the same order as the heats of neutralization already given.

The values found for pyridine and α-picoline agree fairly well with those obtained by Goldschmidt and Salcher, pyridine, $2.4.10^{-9}$; α-picoline, $4.5.10^{-8}$.

[1] van't Hoff: Vorlesungen, I, 127.

[2] This is, perhaps, to be accounted for in part by the difficulty of preparing a pure γ-salt, that obtained apparently still containing traces of the base, from which it was not possible to rid it by washing with alcohol.

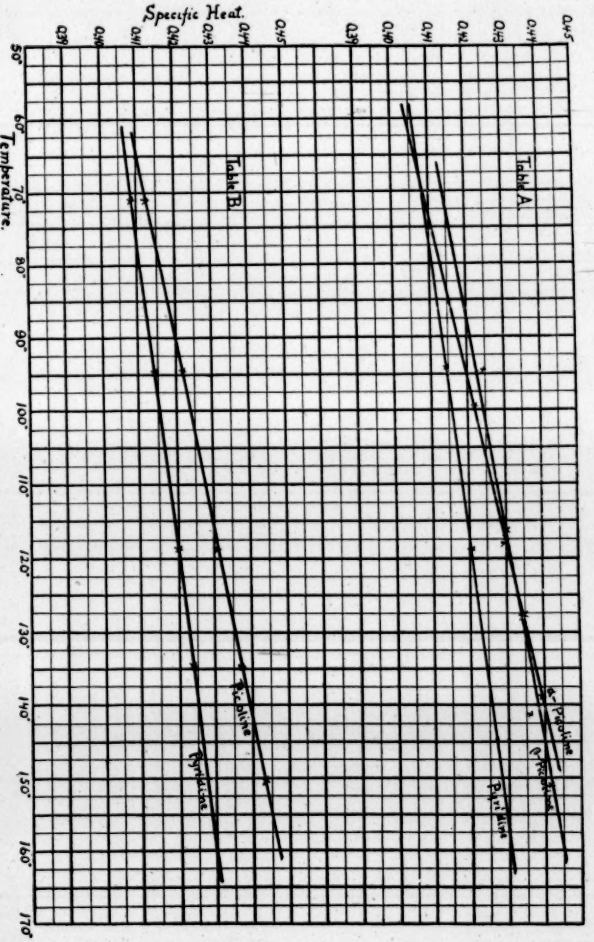
Specific Heat.
0·39
0·40
0·41
0·42
0·43
0·44
0·45
Temperature.
50°
60°
70°
80°
90°
100°
110°
120°
130°
140°
150°
160°
170°
Table A.
Table B.
α-Picoline
β-Picoline
γ-Picoline
Pyridine

Table XV.

Substance.	Density. Brühl. $\frac{20°}{4°}$	Density. C. and W. $\frac{15°}{4°}$	n_{Na} = specific refraction. Brühl. $t.$	Brühl. $n.$	C. and W. $t.$	C. and W. $n.$	$\left(\frac{n^2-1}{n^2+2}\right)\frac{M}{d\frac{t}{4°}} = m$ = mol. refraction. Brühl.	C. and W.
Pyridine	0.9800	0.9893	18°.6	1.51026	17°.3	1.51068	24.09	23.94
α-Picoline	0.9451	0.9497	16°.7	1.50293	17°.1	1.50237	28.98	28.95
"	....	....	....	....	18°.0	1.50225	....	28.95
β- "	0.9579	0.9613	24°.0	1.50432	18°.1	1.50720	28.83	28.83
γ- "	....	0.9571	....	....	17°.0	1.50640	....	28.92

MOLECULAR REFRACTION OF THE PYRIDINE BASES.

In order to further test the condition of purity of our substances, we made use of the simple and accurate method of Pulfrich, whereby the refractive index of the substance under consideration is obtained, from which, in turn, the molecular refraction can be calculated. Brühl, in his classical researches in this direction, had already measured the refractive indices of pyridine, α- and β-picoline.[1] It pleases us to be able to confirm his results in every particular, as a glance at the comparative table shows:

Summing up the results of the above investigation, we arrive at the following conclusions:

(1) That the regularity in the increase of the heats of combustion between homologues, observed in the aliphatic and aromatic series extends also to the pyridine compounds, being found equal to 156 cal. for each CH_2.

(2) That the heat of formation of pyridine and its homologues can be approximately calculated from the formula,

$$C_nH_{2n-5}N = -51.7 \text{ cal.} + n7 \text{ cal.}$$

(3) That Trouton-Schiff's rule $\frac{MH}{T} = \text{constant}$, holds good for the pyridine series also.

(4) That the affinities of pyridine and the picolines are of approximately the same order as that of *p*-toluidine.

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SWITZERLAND,
July, 1902.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON THE "BECKMANN REARRANGEMENT."[2] II.

BY JULIUS STIEGLITZ.

The molecular rearrangement which has come to be known as the "Beckmann rearrangement" has been produced in three classes of nitrogen derivatives: The acid halogen amides, RCON*H(Hal), the oximes of ketones, aldehydes,

[1] Ztschr. phys. Chem., 16, 214.

[2] The first paper was published in this JOURNAL, 18, 751 (1896).

acid salts, amides, and esters, RR'C : N*OH),[1] and the acid azides,[2] RCON*(N_2). In every case the essential point of the rearrangement is that the alkyl (alphyl) group, R, is made to leave the carbon atom which holds it in the original substance and is then found joined to the nitrogen atom, N*, derivatives of an alkyl (alphyl) amine being formed. The following instances may be used in illustration: Acid bromamides on treatment with silver carbonate,[3] alkalies,[4] or sodium methylate[5] produce cyanates, carbamates, and urethanes, respectively:

$$2RCONHBr + Ag_2CO_3 \rightarrow 2CO : NR + 2AgBr + H_2O + CO_2;$$

$$RCONHBr + xKOH \rightarrow KOCONHR + KBr + H_2O;$$

$$RCONHBr + NaOCH_3 \rightarrow CH_3OCONHR + NaBr.$$

Acid azides, on warming with alcohols, give urethanes:[6]

$$RCON(N_2) + HOCH_3 \rightarrow CH_3OCONHR + N_2.$$

The dry alkali salt of an acylhydroxamic acid breaks down spontaneously, yielding an isocyanate:[7]

$$RC(OK) : N(OCOR') \rightarrow CO : NR + KOCOR'.$$

Ketoximes, on treatment with certain dehydrating reagents, give acid amides:

$$RR'C : NOH \rightarrow R'CONHR.$$

The determination of the essential cause and mechanism of these rearrangements is a problem of deepest interest which still awaits its final solution, although it has already been the subject of some investigation and speculation. In a paper published in this JOURNAL six years ago the author developed a theory as to the nature and cause of the rearrangement, and

[1] R' may be hydrogen, an alkyl, an alphyl, an alkoxyl group, a metaloxyl group, OMe', or an amide group.

[2] An alkyl azide, benzylazide, also has been found to react in the same fashion. Curtius: J. prakt. Chem., **63**, 429 (1901).

[3] Hofmann: Ber. d. chem. Ges., **15**, 412 (1882).

[4] Hoogewerff and van Dorp: Rec. trav. chim. Pays-Bas, **8**, 200 (1887).

[5] Lengfeld and Stieglitz: This JOURNAL, **15**, 214, 504 (1893).

[6] Curtius: Ber. d. chem. Ges., **27**, 778 (1894); J. prakt. Chem., **50**, 289 (1894).

[7] Unpublished results of Dr. L. W. Jones, of this university. See also Hantzsch: Ber. d. chem. Ges., **27**, 1256 (1894); Thiele: Ann. Chem. (Liebig), **309**, 189 (1899).

outlined certain points of attack which promised to lend themselves to the experimental investigation of the correctness of the theory. The work has progressed very slowly, largely because an important part was undertaken in collaboration with Mr. E. E. Slosson, of the University of Wyoming, and the latter was able to devote only his summer vacations to the prosecution of the investigation. The work with Mr. Slosson having now reached a certain stage of completeness, it is proposed in this paper to consider the present aspect of our knowledge of the "Beckmann rearrangement" on the basis of all the general facts known in connection with it, and particularly on the basis of the results obtained with Mr. Slosson, as well as in shorter investigations carried out with Drs. O. Folin, H. H. Higbee, H. N. McCoy, J. H. Ransom, and Elizabeth Jeffreys.[1]

It may be said that any interpretation of the "Beckmann rearrangement" must take cognizance of these fundamental points:

(1) The nature of the rearrangement of the three classes of nitrogen derivatives described above seems to be substantially the same. This follows from the strictly analogous character of the initial substances, from the adaptation of the reagents used in effecting the rearrangement to the variation in the elements combined with the nitrogen in the compounds used, and from the frequent identity and otherwise close relationship of the products obtained from all three classes of compounds.

(2) The rearrangement is produced by reagents which stand in the most intimate relation to the elements combined with the nitrogen in each of the classes of nitrogen compounds under investigation. In the case of the acid halogen amides, RCONH(Hal), the effect is produced by substances which have the greatest affinity for the halogen acids—for instance the alkalies and silver carbonate—and salts of these acids are always obtained in the reaction. The halogen atoms go from the condition of "hypo-acid" radicals[2] into simple negative

[1] Beckmann: Ber. d. chem. Ges., **19**, 988, etc. (1886).
[2] Seliwanow: *Ibid.*, **25**, 3620 (1892).

ions and their salts. Van Dam[1] has shown, in fact, that the velocity of the rearrangement is proportional to the concentration of hydroxyl ions in the solution. The rearrangement of the oximes of ketones, aldehydes, and acid esters is effected by dehydrating reagents, water or derivatives of water resulting.[2] The rearrangement of the acylhydroxamic acids, $RCONH(OCOR')$, on the other hand, is again caused by alkalies, salts of the organic acids, $HOCOR'$, being formed. Finally, the rearrangement of the acid azides, $RCON(N_3)$, requires no such reagent; it is produced essentially by the action of heat, nitrogen being evolved in all such cases.

(3) When in the case of the acid bromamides, $RCONH^*Br^*$, the possibility of the loss of hydrobromic acid by the union of the atoms marked * in the formula is cut off by replacing the hydrogen atom by an alkyl or an alphyl group, the tendency to undergo the "Beckmann rearrangement" has been found also to be entirely suppressed. Mr. Slosson and I have shown this to be the case for the acylalkylhalogenamines[3] whose constitution we determined by the preparation of identical substances by the action of hypochlorous acid on acetylamylamine, on the one hand, and of acetic acid anhydride on chloramylamine, on the other hand:

$$CH_3CONHC_5H_{11} + HOCl \rightarrow CH_3CONCl(C_5H_{11}) + H_2O.$$

$$(CH_3CO)_2O + C_5H_{11}NHCl \rightarrow CH_3CONCl(C_5H_{11}) + C_2H_4O_2.$$

Chlorimidoesters, $RC(:NCl)OR'$, also have lost the tendency[4] to suffer the molecular rearrangement so characteristic of the parent substances, the acid halogenamides. In like fashion, according to an investigation carried out by Dr. Higbee, at my suggestion, derivatives of the oximes, in which the possibility of the breaking off of water from a trivalent nitrogen atom is excluded, refuse to undergo the rearrangement when treated with the same dehydrating reagents which

[1] Rec. trav. chim. d. Pays-Bas., **18**, 408 (1899); **19**, 318 (1900). In the same investigation Van Dam proved that the reaction is a monomolecular one, the rearrangement, therefore, intramolecular.

[2] See this JOURNAL, **18**, 754 (1896). Foot-note.

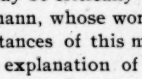
[3] See the article in a later number of this JOURNAL, and preliminary reports: Ber. d. chem. Ges., **28**, 3266 (1895); **34**, 1613 (1901).

[4] *Loc. cit.*, and Stieglitz, This JOURNAL, **18**, 751 (1896).

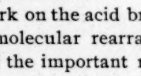
are so effective in the case of the ketoximes. β-Benzoyl-β-phenylhydroxylamine, $C_6H_5CON(C_6H_5)OH$, under such treatment does not give the least discernible trace of diphenylamine, and yet the color test for this substance belongs to the most sensitive known in organic chemistry.

On the basis of these general facts and with the aid of a number of other experimental facts which will be referred to in the course of the discussion, the most important of the theories advanced in explanation of the "Beckmann rearrangement" may be critically considered.

A. W. Hofmann, whose work on the acid bromamides gave us the first instances of this molecular rearrangement, never suggested any explanation of the important reaction he discovered. Hoogewerff and van Dorp,[1] who continued Hofmann's work with great skill, advanced the first hypothesis as to the nature and cause of the rearrangement of the acid bromamides, to whose alkali salts they assigned the constitution, RCO(NMe'Br). By intramolecular migration the salt



is supposed to be transformed into



which in turn is decomposed into potassium bromide and an isocyanate. The transposition is said to be caused, in particular, by the tendency of nitrogen to combine with radicals more positive than the halogens. In support of their view these chemists point out that the intramolecular migration must depend largely on the nature of the group R. When this group becomes more negative the transposition must become more difficult. Observations made at the time the theory was advanced confirmed this conclusion; the salts of the nitrobenzbromamides were found to be more stable than those of benzbromamide. It was found later, however, by McCoy and myself,[2] that dibromsalicylicbromamide, in which R is the exceedingly negative radical $C_6H_2Br_2(OH)'$, suffers the rearrangement even below 5°, in the course of a few sec-

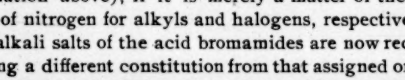
[1] Rec. trav. chim. Pays-Bas., **6**, 373 (1887); **8**, 173, etc. (1889) They were the first to call attention to the similarity of Hofmann's reaction and the "Beckmann rearrangement" of the oximes. See also: Graebe and Rostovzeff: Ber. d. chem. Ges., **35**, 2747 (1902); Hantzsch: *Ibid.*, **35**, 3579 (1902).

[2] This JOURNAL, **21**, 116(1899).

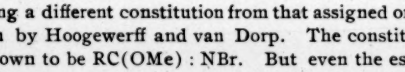
onds, so rapidly that the bromamide could not be isolated. Van Dam,[1] in Hoogewerff and van Dorp's laboratory, obtained exactly the same results working at —12°, independently of, and almost simultaneously with, the work done in this laboratory. As to the main point in Hoogewerff and van Dorp's hypothesis, the theory fails to adapt itself to the entirely analogous behavior of the acid azides and acid bromamides, and to explain the fact that acylalkylhalogenamines do not rearrange.[2] One would expect the intramolecular transposition of the bromine and the alkyl R, as in

to occur quite as easily as in the case of the alkali salts (see the equation above), if it is merely a matter of the relative affinity of nitrogen for alkyls and halogens, respectively.

The alkali salts of the acid bromamides are now recognized as having a different constitution from that assigned originally to them by Hoogewerff and van Dorp. The constitution[3] is now known to be RC(OMe) : NBr. But even the esters corresponding to such salts, the chlor- and bromimido esters, do not undergo the "Beckmann rearrangement." The reactions



and



would be strictly analogous, according to the Dutch chemists' interpretation, but the second reaction does not take place. In conclusion, the important function of the reagents which produce the rearrangement of the acid bromamides (see page 51), seems to find no place in this theory.[4]

[1] *Loc. cit.*

[2] Stieglitz and Slosson: *Loc. cit.*

[3] See below, page 64.

[4] NOTE: In a short article (Ber. d. chem. Ges., **35**, 3579 (1902)) published after this paper was written, Hantzsch, while accepting Hoogewerff and van Dorp's in-

Beckmann, the discoverer of the molecular rearrangement of the oximes of ketones and aldehydes, whose name is now used to designate this typical transformation, advanced an explanation[1] of the reaction in 1894, which is very much like the one just discussed. He suggested, rather vaguely, that the rearrangement might consist simply in the transposition of electrically charged radicals or ions, and that the dehydrating reagents employed act chiefly, although not wholly, as catalytic agents giving the necessary impetus for a change from a labile to a stable condition. In the reaction

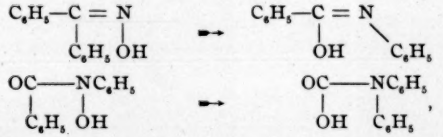
$$(C_6H_5)_2C:NOH \rightarrow C_6H_5C(OH):NC_6H_5$$

a direct exchange of the phenyl and hydroxyl groups is assumed. The theory is essentially a restatement of obvious results obtained with only one class of compounds, the oximes. Like the previous theory, it fails to explain, on the one hand,

terpretation of the rearrangement, suggests that the rearrangement of the acid bromamides is caused by an alkali essentially because the latter is necessary to produce a double bond between the acyl carbon and the nitrogen. Whereas the acid bromamides have the constitution, RCO.NHBr, the salts have the constitution RC(ONa):NBr, (see page 64), which is said to bring them into much closer analogy with the oximes. The rearrangement is supposed to proceed then by an exchange in position of the alkyl R, and the bromine atom. This possibility that a double bond might be an essential condition for the rearrangement, and might explain best the rearrangement of the stereoisomeric oximes was the chief reason for the study of the chloro- and bromimido esters, RC(OR):NHal, by the author (see the first paper, this JOURNAL, **18**, 751 (1896), and the article by Mr. Slosson in a later number of this JOURNAL). They were found to be remarkably stable nitrogen halides which not only do not suffer a "Beckmann rearrangement" spontaneously at ordinary temperatures (as do the salts of the acid bromamides), but they do not even rearrange on warming to 100° to 140°. In fact, they have never, as yet, been observed to rearrange under any condition whatsoever. Stereoisomers do not seem to exist, and preliminary experiments, which will be continued by Mr. Test, indicate that the acid chloramides produce, on the one hand, with diazomethane the stable chlorimido esters, and, on the other hand, with alkalies the easily rearranged salts. These facts show that the double bond is, after all, not the vital factor that Hantzsch assumes, and that the effect of the alkali must be something essentially more than to produce a double bond. The ready and sometimes spontaneous rearrangement of acylhydroximic acid salts, RC(ONa):NOAcyl, and the marked stability of the corresponding esters, RC(OR'):NOAcyl, (the acetyl ester of ethylsynbenzhydroximic acid can be heated to 140° without change, according to Werner: Ber. d. chem. Ges., **25**, 41 (1892)), emphasize the same point. Hantzsch's assumption of the intermediate formation of a chlorimide, $R_2C:NCl$, in the rearrangement of the ketoximes under the influence of phosphorus pentachloride also appears unwarranted in view of the above facts, and in view of the further fact that other acid dehydrating reagents have the same effect. Finally, the acyl azides have no double bond between carbon and nitrogen and yet they are rearranged with remarkable smoothness.

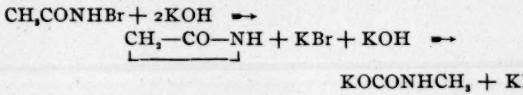
[1] Ber. d. chem. Ges., **27**, 300 (1894).

the analogous behavior of the oximes and acid azides, and, on the other hand, the complete difference in behavior of compounds most closely allied to the oximes, such as β-benzoyl-β-phenylhydroxylamine. There is no evident reason, according to Beckmann's view, why both the following reactions should not occur with equal ease:



and yet the second reaction does not take place even to a slight extent. Finally, the characteristic adaptation of the reagent effecting the rearrangement to the class of nitrogen compounds used (see page 51), is also left practically out of consideration in this interpretation.

In an unpublished investigation carried out at this university in 1896, Dr. Bernhard C. Hesse examined experimentally the reliability of an entirely new explanation of the "Beckmann rearrangement," based on the following views: It was thought possible that the transformation of acetbromamide, for instance, was accomplished through the following stages:



The intermediate formation of a triatomic ring was the basis of the explanation, in analogy to similar known changes of position of alkyls through the intermediate formation of trimethylene rings. Dr. Hesse has kindly consented to let me publish the results of this investigation.

The reliability of the theory was tested by studying the rearrangement-product of trimethylacetbromamide, $(CH_3)_3C.CONHBr$. An intermediate triatomic ring formation being impossible in this case, at best a tetratomic ring could result. In the latter event isobutylamine, $(CH_3)_2CHCH_2.NH_2$, would

be the final product, while if no ring formation at all occurred, tertiary butylamine, $(CH_3)_3C.NH_2$, would be formed. Dr. Hesse identified the salts obtained as those of tertiary butylamine, thus disposing of the possibility that intermediate unstable ring formations of the nature indicated are the cause of the rearrangement.

It may be added that a triatomic ring, as used in the above equation would, doubtless, open between the carbonyl and the imide groups, as all acid amides are saponified in this way.

Only a very brief reference need be made to the views of Freundler.[1] He suggests that the rearrangement of the acid bromamides could be due to a series of reactions, the essential feature of which is the intermediate formation of carbylamine and hypobromite. These views were suggested by the erroneous idea that an isocyanate had never been isolated as an intermediate product in Hofmann's reaction. It is hardly necessary to add that none of Freundler's supposed intermediate products have ever been isolated in the reaction under discussion, and that it would be impossible to bring his views into accord with the behavior of the acid azides and the acylhydroxamic acid salts.

The most recent suggestion as to the nature of the "Beckmann rearrangement" has been made, incidentally, by Nef[2] in connection with an exhaustive study of dissociation phenomena of alcohols, ethers, and organic acid salts. Having shown that an alkylidene residue, RCH=, or a phenylene group, $C_6H_4=$, is often broken off from one of the above compounds, and sometimes absorbed again in a different position from that occupied in the original molecule, Nef suggests that the rearrangement of the acid bromamides and of the oximes is due to similar changes. For instance, acetbromamide is supposed to undergo the following series of changes:

$$CH_3CONHBr \rightarrow CH_3:+HCONHBr \rightarrow$$
$$HCO(NCH_3Br) \rightarrow OC:NCH_3+HBr.$$

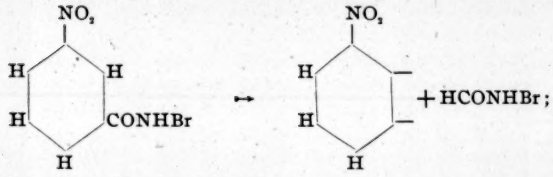
Further close investigation may, possibly, be needed abso-

[1] Bull. Soc. Chim., 17, 421 (1897).
[2] Ann. Chem. (Liebig), 298, 308 (1897); 318, 39, 227 (1901).

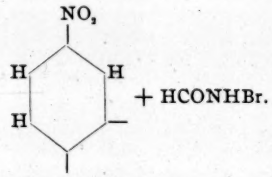
lutely to prove or disprove the correctness of this interesting view and, with the consent of Dr. Nef, experiments lending themselves to a further test of the theory will be carried out. At present, however, it may be said that it cannot be applied directly to the acid azides, and that it leaves quite out of consideration the fact that the nature of the reagents, used to effect the molecular rearrangement in each of the three classes of compounds under discussion, stands obviously in closest relation to the elements or groups combined with the nitrogen, and not to the alkyl or alphyl group attached to the acyl carbon atoms (see page 51). The most important difficulty, however, in the way of Nef's view is that in every product of the "Beckmann rearrangement" known to the author, the nitrogen atom is found to occupy exactly the same position in the alkyl chain or alphyl nucleus which was held originally by the carbon atom that separated the migrating alkyl or alphyl group from the nitrogen atom. Thus, trimethylacetbromamide, $(CH_3)_3C.CONHBr$, according to the work of Dr. Hesse reported above, gives tertiary butylamine, $(CH_3)_3C.NH_2$, and not isobutylamine, $(CH_3)_2CHCH_2NH_2$, and the three nitrobenzbromamides, para, meta, and ortho, give the corresponding para-, meta-, and orthonitranilines or their derivatives.[1] This is not necessary and hardly possible always, according to Nef's view, for derivatives of tertiary and aromatic acids, ketones and aldehydes are supposed by him to dissociate into olefines or phenylenes,[2] as the methylene dissociation is excluded, and these residues are said to act as the methylene does in the above reaction. Under such circumstances one would have to expect that metanitrobenzbromamide would give, to a considerable extent, the same aniline derivatives as either ortho- or paranitrobenzbromamide, from the reactions :

[1] Hoogewerff and van Dorp : Rec. trav. chim., Pays-Bas, **8**, 193, 196, 199 (1889) ; Lengfeld and Stieglitz : This JOURNAL, **16**, 371 (1894) ; Folin : *Ibid.*, **19**, 325, etc., (1897); Swartz ; *Ibid.*, **19**, 303 (1897) ; Jeffreys : *Ibid.*, **22**, 41 (1899) : Struve and Radhausen : J. prakt. Chem., **52**, 230 (1895).

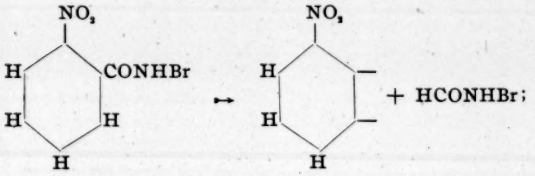
[2] Nef : *Loc. cit.*

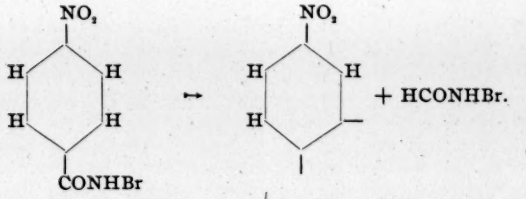


or



The same intermediate nitrophenylene must result as from either one or the other of the following dissociation reactions:





But, as a matter of fact, each nitrobenzbromamide gives exclusively an excellent yield of the corresponding nitraniline

or its derivatives.[1] Whether traces or very small quantities of the isomers are also formed remains a question for further investigation. One would expect, however, not traces but considerable quantities of identical substances in view of the above discussion.

The actual dissociation tendency of compounds of the general type, RR'NX, in which X is a halogen, a hydroxyl or an acid group, RCO, as will be shown below, has been observed in a number of instances to be rather toward the breaking off of R'X from the molecule, leaving most likely an unsaturated imide group with univalent nitrogen, RN=, as a primary but unisolated product of dissociation. Such a result would be analogous to the alkylidene formations exhaustively studied by Nef. It seems at present, therefore, that the conceptions of "methylene and phenylene dissociations" will aid in clearing up the problem of the "Beckmann rearrangement" rather by analogy than by direct application.[2]

The last interpretation of this molecular rearrangement to be discussed is that proposed by the writer in 1896, the experimental study of which forms the basis of this paper. It may be briefly stated as follows: Starting out from the pronounced similarity in the behavior of the parallel classes of derivatives, RCONHBr, (I.), RCONH(OCOR) (II.), or $R_2C(NOH)$, (II'.), and $RCON(N_2)$, (III.), an initial change which could be common to all three classes of compounds was sought and found in the possibility of all three series of compounds easily yielding an identical intermediate derivative (for instance, (RCO)N=), with univalent nitrogen. The first class would do so by the initial loss of hydrobromic acid; the second, (II.), by the loss of an organic acid, HOCOR, or (II'.), by the loss of water from salts[3] such as the hydrochlorides, $R_2CCl.NHOH$, the result being $R_2CCl.N=$; the third, simply by that loss of nitrogen which is so common with diazo derivatives.

The nature of the reagents used to effect the rearrangement is in complete agreement with this conception, alkalies being

[1] See Folin: *Loc. cit.*
[2] See the note by Nef: This JOURNAL, 18, 753 (1896).
[3] See, the first paper, *Loc. cit.*

used for both (I.) and (II.), acid dehydrating reagents for (II'.), and essentially heat only for (III.). It is the intermediate product, such as RCO.N=,[1] which is considered to suffer the molecular rearrangement proper, owing to the potency of the free valences of univalent nitrogen. For instance

$$\begin{matrix} OC{-}N \\ | \quad \wedge \\ R \end{matrix} \rightarrow \begin{matrix} OC{-}NR \\ | \quad | \end{matrix} \rightarrow OC{=}NR$$

an isocyanate is formed in this case as the first tangible product.[2]

According to this interpretation, the rearrangement should not be possible if, for instance, in the acid bromides the loss of hydrobromic acid is prevented by replacing the hydrogen atom by an alkyl or an alphyl group. The work with Mr. Slosson has proved that such is actually the case, neither series of derivatives of the acid bromides, RCO(NR'Br) and RC(OR')NBr, undergoing the change in question. Likewise, it will be remembered, Dr. Higbee found that oximes, RCO.(NC_6H_5)OH, which cannot lose water in the way described, show no tendency whatever to undergo the "Beckmann rearrangement." The interpretation is, therefore, in agreement with the three most striking fundamental characteristics of the rearrangement.

It is also in complete accord with the most recently discovered cases of a "Beckmann rearrangement," *viz.*, that of benzylazides, according to[3]

$$C_6H_5CH_2N.(N_2) \rightarrow C_6H_5CH_2N: + N_2 \rightarrow CH_2{=}NC_6H_5 + N_2.$$

Not one of the other theories proposed can account for this additional instance of a "Beckmann rearrangement."

In further support of the views expressed, the following instances will be mentioned in which the formation of univalent nitrogen derivatives from the classes of compounds under discussion is clearly indicated :

[1] Tiemann, I find, expressed, incidentally, a similar view in regard to one of the above classes of compounds. Ber. d. chem. Ges., **24**, 4163 (1891).

[2] Hofmann: Ber. d. chem. Ges., **15**, 411, 412 (1883). Hantzsch: *Ibid.*, **27**, 1256 (1894). Thiele: Ann. Chem. (Liebig), **309**, 189 (1889). Dr. L. W. Jones, this laboratory, private communication. See Graebe: *Loc. cit.*

[3] Curtius: J. prakt. Chem., **63**, 428 (1901); Ber. d. chem. Ges., **35**, 3229 (1902).

a. An exhaustive study of the many remarkable reactions of β-phenylhydroxylamine and its homologues has led Bamberger[1] to the conclusion that a phenylimide is the first unisolated product from which many varied derivatives are obtained. For instance, on heating β-phenylhydroxylamine, azobenzene and water are the chief products of decomposition, a reaction which may be interpreted:

$$C_6H_5NHOH \rightarrowtail C_6H_5N{=} + H_2O$$

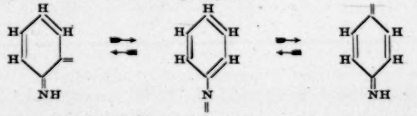
and

$$2C_6H_5N{=} \rightarrowtail C_6H_5N = NC_6H_5.$$

At the same time, the characteristic odor of a carbylamine, RNC=, is developed exceedingly strongly. As an ordinary carbylamine can hardly be produced under these circumstances, the suspicion is aroused that the odor is due to small quantities of the analogous phenylimide, $C_6H_5N{=}$, escaping instantaneous condensation.[2]

[1] Ber. d. chem. Ges., **27**, 1550 (1894); **33**, 3600 (1900); **34**, 61 (1901).

[2] NOTE.—It seems very probable, however, that phenylimide, as soon as formed, goes over, partly, into the isomeric imidophenylenes:

I. 

and it remains a question, therefore, to which of these substances the carbylamine odor is really due.

This conception of the partial isomerization of phenylimide seems to me to give a better interpretation than Bamberger's of all of the reactions of phenylhydroxylamine discussed and investigated so brilliantly by Bamberger (*Loc. cit.*), in which the para (or ortho) position of the phenylimide enters into action. It accounts for the great and varied reactivity of the para-position in taking up, additively, many compounds, such as water, alcohols, anilines, phenols, etc. It also explains, readily, one reaction, which even Bamberger found particularly peculiar and difficult to understand (Ber. d. chem. Ges., **34**, 62), namely, the change of phenylhydroxylamine into paraoxydiphenylamine, on being heated with dilute sulphuric acid; the partial saponification to a phenol derivative which Bamberger could hardly account for, is accomplished at the imidophenylene stage of the reaction:

$$=C_6H_4:NH + H_2O \rightarrowtail =C_6H_4:O + NH_3$$

$$=C_6H_4:O + H_2NC_6H_5 \rightarrowtail C_6H_5NH\!\!>\!\!C_6H_4:O \rightarrowtail C_6H_4NHC_6H_4OH$$

(For the formation of aniline, see Ber. d. chem. Ges., **33**, 3605 and 3617.)

It may be added that with the help of Bamberger's fine work and ideas the conception developed here gives us, at last, a complete explanation of the "benzidine rearrangements" of the hydrazines. It is noteworthy that these rearrangements are very easily effected by the agency of even dilute acids, a fact readily understood from the following:

b. Chattaway and Orton[1] have found, likewise, that phenylchloramine, C_6H_5NHCl, breaks down readily into hydrochloric acid and azobenzene, and phenylbromamine still more readily into hydrobromic acid and azobenzene.

c. The same chemists[2] and Slosson[3] have found that benzoylphenylchloramine, $C_6H_5CO.N(C_6H_5)Cl$, gives, on being heated, some benzoyl chloride[4] (besides forming chiefly *p*-chlorbenzanilide). In this connection, it is interesting to note that the action of aqueous alkali on the acylalphylhalogen amines, $RCON(C_6H_5)Cl$, while producing an acylanilide as the chief product, was invariably observed by Slosson and myself to be accompanied by the formation of an unknown compound with the pungent carbylamine odor.[5]

d. By the action of phosphorus pentachloride on β-benzoyl-β-phenylhydroxylamine, $C_6H_5CO.N(C_6H_5)OH$, Dr. Higbee has found that some benzoyl chloride is formed and again the inevitable carbylamine odor was most pronounced. Treatment of the same substance with acetic anhydride likewise produced this characteristic odor.

e. The reduction products of the acylazides also indicate

II. $C_6H_4NH.NHC_6H_5 + HX \rightarrowtail C_6H_5N= + C_6H_5NH_2X.$

III. $C_6H_4N= \rightleftarrows =C_6H_4:NH.$ (Para and ortho; see I.)

IV. $p\text{-}NH:C_6H_4= + C_6H_5NH_2 \rightarrowtail NH:C_6H_4\langle^{H}_{C_6H_4NH_2} \rightarrowtail p\text{-}H_2N.C_6H_4.C_6H_4.NH_2.$

("Benzidine rearrangement.")

V. $o\text{-}HN:C_6H_4= + C_6H_5NH_2 \rightarrowtail o\text{-}H_2N.C_6H_4.C_6H_4NH_2$ (p)

("Diphenylene rearrangement.")

VI. $NH:C_6H_4 + H_2NC_6H_5= \rightarrowtail HN:C_6H_4\langle^{H}_{NHC_6H_5} \rightarrowtail H_2N.C_6H_4NHC_6H_5.$

("Semidine rearrangement.")

VII. $2C_6H_4N= \rightarrowtail C_6H_5N:NC_6H_5.$ (Azobenzene formation.)

We find, thus, all the interesting products of this important action fully accounted for. These simple interpretations give us a further instance of the usefulness of the conceptions of univalent nitrogen derivatives as intermediate products in molecular rearrangements whose explanation has always proved so baffling to chemists.

[1] J. Chem. Soc. (London), **79**, 462 (1901). Similar cases are described in the same paper.

[2] *Ibid.*, **75**, 1053 (1899).

[3] *Loc. cit.*

[4] The nature of the corresponding nitrogenous dissociation-product has not been determined, as yet. The reaction will be studied further.

[5] Slosson: *Loc. cit.*

an intermediate formation of the elusive univalent nitrogen derivatives.[1]

f. Curtius[2] deduces the formation of the main decomposition products of benzylazide from the rearrangement of benzylimide, $C_6H_5CH_2N=$.

In the first paper on the "Beckmann rearrangement," mention was made of the fact that no determination had been made of the constitution of the metal salts of the acid halogen amides which are formed before the rearrangement is effected.[3] The two forms, RCO.(NMe Hal), (I.), and RC(O Me)(N Hal), (II.), were considered possible. This determination has since been made by Dr. Ransom and myself,[4] and by Hantzsch.[5] Ransom and I have found that diazomethane converts benzchloramide into methyl chlorimidobenzoate,[6] according to

$$C_6H_5CONHCl + CH_2N_2 \rightarrowtail C_6H_5C(:NCl)(OCH_3) + N_2.$$

The salts of the acid chloramides, accordingly, have the constitution (II.), corresponding to this ether. We also found that benzchloramide could be titrated quantitatively with a standard alkali, using phenolphthalein as the indicator.

A little later, both of these results were also obtained, independently, by Hantzsch; the latter showed by his elegant method of investigation that the free acid halogen amides are not true acids, that the metal derivatives, however, are the salts of true and not very weak acids, and consequently derivatives of a substance of different constitution from the free halogen amides. By analogy to certain corresponding ketones and nitro compounds, Hantzsch assigns to the salts the constitution, (II.), as salts of an unstable hydroxyl acid,

[1] Stieglitz: This JOURNAL, **18**, 753 (1896).

[2] *Loc. cit.*

[3] Stieglitz: *Loc. cit.*

[4] Preliminary note, Ber. d. chem. Ges., **34**, 1615 (1901).

[5] *Ibid.*, **35**, 228 (1902).

[6] The ester was isolated by distillation and characterized by its action on hydriodic acid and on ammonia. By reduction with hydrogen chloride in ligroin solution it gave the hydrochloride of methyl imidobenzoate, $C_6H_5C(NH)OCH_3.HCl$. This salt gave, on being heated, methyl chloride and benzamide, and, on treatment with water, it gave methyl benzoate and ammonium chloride. Finally, treatment of the original chlorimide with hydrogen sulphide and distillation of the product with alkali failed to give even a trace of methylamine, which showed that the isomeric methyl derivative had not been formed even in traces.

RC(OH) (N Hal), to the neutral parent substance the constitution of an amide, RCO.NH Hal. It is evident that the two methods of experimentation, the physico-chemical and the organo-synthetic, supplement each other in a desirable fashion.

This not unexpected result of the determination of the constitution of the salts of the acid bromamides does not affect the interpretation of the "Beckmann rearrangement" as given above; the change

$$RC(OK):NBr \rightarrowtail RCO.N:+KBr$$

is quite normal in view, notably, of Thiele's[1] work on dissociation and addition reactions involving two even more widely separated atoms in a molecule than are the nitrogen and oxygen atoms in the salts of the acid bromamides.

The constitution of the salts also suggests, however, a loss of potassium bromide and the possible formation of a ring compound, $RC:\underset{\llcorner\!\!-\!\!-\!\!\lrcorner}{NO}$, rather than a univalent nitrogen derivative as the intermediate product which actually suffers the molecular rearrangement. The strain in the triatomic ring, rather than the reactivity of univalent nitrogen, would then be the ultimate cause of the rearrangement:

$$C_6H_5C\overset{N}{\underset{O}{<}} \rightarrowtail CO:NC_6H_5.$$

Such a suggestion has been made, incidentally, by Hantzsch[2] in explanation of the rearrangement of the acetate of benzhydroxamic acid, and Baeyer[3] has expressed a similar view in connection with the transformation of ketone peroxides into lactones. It may be said here that such an interpretation could be made even far more general: as the compound, RCO.N=, could very readily go over into the isomeric ring derivative, many of the facts in favor of the formation of the former would obviously hold for the latter. The behavior of the acid bromamides, the hydroxamic acid salts and, possibly,

[1] Ann. Chem. (Liebig), **396**, 87 (1899).

[2] Ber. d. chem. Ges., **27**, 1256 (1894). For Hantzsch's most recent views, see note, page 54.

[3] *Ibid.*, **32**, 3627 (1900).

of the acid azides, the contrasting behavior of the substituted acid halogen amides and hydroxamic acids, $RCONC_6H_5(OH)$, would be in equally good agreement with both interpretations. But, after all, the following facts favor decidedly the more comprehensive idea of the agency of univalent nitrogen.

a. Amidoximes, $RC(NOH)NH_2$, undergo the rearrangement[1] under the influence of acid dehydrating reagents as do other oximes. An intermediate ring compound, $RC{=}N{-}NH$, an isodiazomethane, and a hydrazine would tend to give hydrazine[2] or to change, if at all, into its closely related isomer, a diazo methane, $RCH{-}N{=}N$, and give the latter's decomposition products, nitrogen and an alkylidene derivative, rather than suffer a separation of two carbon atoms from each other, and two nitrogen atoms from each other, against their well-known tendencies. On the other hand, the reactions

$$\begin{aligned} RCCl(NH_2)NHOH &\rightarrowtail RCCl(NH_2).N{=}+H_2O, \\ &\rightarrowtail CCl(NH_2):NR+H_2O, \\ &\rightarrowtail CO(NH_2)NHR+H_2O, \end{aligned}$$

introduce no new assumption into the theory of the activity of univalent nitrogen—they appear as entirely normal.

b. The ring theory cannot be applied to the rearrangement of the ketoximes until an N-alkyl (alphyl) aldoxime or ketoxime, $R_2C.NR'{-}O$, has been made to suffer a "Beckmann rearrangement" with a migration of an *alkyl* or an *alphyl* group, R, since such a ring $R_2C{-}NH{-}O$ would have to be the cause of the rearrangement of the ketoximes.[3] Such a migration does not appear on record, although the "Beckmann reagents" have been applied to such oximes.[4]

c. According to Werner,[5] the hydroximic acid chlorides,

[1] Tiemann: Ber. d. chem. Ges., **24**, 4162 (1891).
[2] See, Hantzsch: *Ibid.*, **34**, 2507 (1901).
[3] See, Baeyer: *Loc. cit.*
[4] *e. g.*, Beckmann: *Ibid.*, **26**, 2272 (1893).
[5] *Ibid.*, **32**, 1654, 1975 (1899). See these papers for the actual condensation-products.

$RCCl(NOH)$, and benzoates, $RC(O.OCC_6H_5)(:NOH)$, in which the ready formation of the above ring appears particularly well favored, do lose acid easily but no rearrangement ensues.

d. The ring theory is utterly incompatible with the most recent case of a "Beckmann rearrangement," that of benzylazide,[1] $C_6H_5CH_2N(N_2)$, while it appears as a perfectly normal case of a rearrangement of a univalent nitrogen derivative, benzylimide:

$$C_6H_5CH_2N: \rightarrow CH_2:NC_6H_5.$$

Finally, attention is called, once more, to the fact that, whereas there is not a single fact concerning the constitution and reactions of organic compounds known to the author which does not agree perfectly with the theory of the "Beckmann rearrangement" postulating the intermediate formation of a univalent nitrogen derivative, it does not agree so well with the more obscure relations of the theory of stereoisomerism of ketoximes and their influence on the rearrangement of these isomers.[2] It is hoped that future work will remove this difficulty.

The conclusions arrived at may be summed up as follows:

1. The interpretations of the "Beckmann rearrangement" given by Hoogewerff and van Dorp, Hantzsch, Beckmann, Hesse, Freundler, and Nef do not agree with all the facts established in connection with this reaction.

2. All the most important results of the investigations of the reaction from the point of view of the constitutions of the substances involved agree best with that interpretation which postulates the intermediate formation of a univalent nitrogen derivative as the essential cause of this characteristic rearrangement. This conception is comprehensive enough to satisfy all the cases where the rearrangement has been observed actually to occur in widely varied classes of compounds, such as:

[1] Curtius: *Loc. cit.*

[2] See the first paper, *Loc. cit.*

I.	Acid halogen amides:	$RCONH(Hal)$;
II.	Acyloximido acid salts:	$RC(NOAcyl)(OMe)$;
III.	Ketoximes:	$R_2C(NOH)$;
IV.	Oximido acid esters:	$RC(NOH)(OR)$;
V.	Oximido acids:	$RCO.NHOH$;
VI.	Amidoximes:	$RC(NOH)NH_2$;
VII.	Acid azides:	$RCO.N(N_2)$;
VIII.	Benzylazides:	$RCH_2N(N_2)$.

It also satisfies those otherwise analogous cases where the rearrangement, for no other apparent reason than the impossibility of the fulfilment of this condition, could not be effected, such as:

I′.	Acylalkyl (alphyl) halogen amines:	$RCO(NHal\,R')$;
II′.	Halogen imido esters:	$RC(NHal)OR'$;
III′.	Acyl-β-alphylhydroxylamines:	$RCO(NR'OH)$;
IV′.	N-Alkyl (alphyl) ketoximes:	$R_2C(NR'O)$.

3. Whatever interpretation be given of the rearrangement, it seems to have been satisfactorily established that the groups of compounds I. and II. suffer the transformation only when opportunity is offered for the loss of the acids, H(Hal) or HO(Acyl), by the formation of their salts, groups III., IV., V., and VI. when dehydrating reagents are used, VII. when nitrogen is evolved under the influence of heat.

CHICAGO, Oct. 13, 1902.

ON BORATE OF MANGANESE.

BY H. ENDEMANN AND JOHN W. PAISLEY.

Borate of manganese is an article of commerce which is used to quite an extent as a dryer for oils, and one would suppose that the substances sold under such designation would possess a certain uniformity of composition.

As a result of a number of analyses of such commercial articles it was learned that this is not so. The substance which acts as the dryer in this compound is the manganous oxide, which dissolves in the oil, while the boric acid acts merely as a protector of this manganous oxide, preventing its oxidation to manganic oxide, which is not wanted for the reason that it induces oxidation of the oil before it is exposed to the air.

No formula for borate of manganese has been published for the reason that it has not been obtained in a pure state, for water used to remove the salts of the mother-liquor removes not only these but also boric acid and manganese, but mainly the former,[1] with the result that compounds remain which do not contain as much boric acid as would correspond to the supposed formula MnB_4O_7. As the boric acid is removed from the precipitate it commences, even during the washing, to turn brown in the air, owing to the oxidation of the manganous oxide, and if not then, certainly on drying even at the ordinary temperature. To prevent this, manufacturers have employed various means. Some use an excess of borax above that required by the equation

$$MnCl_2 + Na_2B_4O_7 = MnB_4O_7 + 2NaCl,$$

and then do not even wash. They sell, practically, a mixture of chloride of manganese and borax. Others wash, and as the product turns brown, restore the color by the addition of sulphite of soda.

Others again wash and supply the loss of boric acid by the admixture of organic acids. The proper proportion is 71 manganous acid to 139.6 boric acid. Such a compound can be dried in air and heated to 150° C. without changing its color, while all which contain less boric acid will turn brown on drying, especially so at an elevated temperature.

With the foregoing as a guide, the composition of borate of manganese, as it is found in trade, can be understood. The samples examined were partly domestic, partly imported. They contain, according to analysis:

	Boric oxide, B_2O_3.	Manganous oxide, MnO.
1	39.36	12.00
2	40.88	16.19
3	37.38	31.06
4	11.09	6.43

Nos. 1 and 2 contained nearly all the salts produced by the reaction, together with an excess of borax. No. 3 was well washed but had sulphite of soda added to restore the color,

[1] Joulin: Ann. chim. phys. [4], 30, 272.

which sulphite was partially oxidized to sulphate. No. 4 contained a considerable amount of organic resin acids. We will hardly be able to find another product of chemical industry, where, under the same name, substances of such wide divergence in composition are sold.

The question now arose, What is the composition of borate of manganese, which will stand access of air and drying without becoming liable to oxidation? In a recent controversy it was claimed that the composition of borate of manganese, as obtained by precipitation, was $MnO.B_4O_6$, and that the pure article should contain, therefore, 33.7 per cent of manganous oxide and 66.3 per cent of boric oxide. As authority for this we were referred to an article by Prof. Edgar F. Smith, which originally was published in this JOURNAL.[1] We did not find in this publication any analysis of the precipitate referred to. In fact, Prof. Smith had utilized the fact that a 50 per cent alcoholic solution of borax precipitates exactly so much manganese as corresponds to the sodium contained in borax, or, in other words, the sodium contained in borax acts as so much sodium hydroxide under the conditions of the experiment. That the precipitate is not $MnO.B_4O_6$ is evident alone from the fact that it turns brown in the air, which is a certain sign that dissociation had taken place.

By working in an alcoholic solution Prof. Smith had guarded against a loss of manganese, which is an essential condition in his case, but the conditions differ when the precipitation is accomplished in water solution.

While alcohol causes dissociation whereby the precipitate loses boric acid but none of its manganese, water produces dissociation into free boric acid, which is a solvent for the precipitated borate of manganese. We lose, therefore, boric acid as well as manganese. The presence of salts in the mother-liquor causes, likewise, a considerable loss, and among such salts the sulphates are better solvents than the chlorides. For this reason it is better to use chloride of manganese than sulphate of manganese. Sulphate of magnesium, sulphate of manganese, and sulphate of sodium dissolve borate of

[1] This JOURNAL, 4, 279 (1882).

manganese forming solutions which possess an intensely alkaline reaction towards litmus paper. This solvent action is so great that, using sulphate, but 54 per cent washed precipitate was obtained against 68 per cent in the case of chloride. When borate of manganese is treated with water and the solution examined we find that the proportion of the respective substances is $MnO : 3B_2O_3$. Hence the precipitates become richer in manganese and poorer in boric acid.

Of the many analyses made of such washed precipitates we give the following :

I. is obtained by precipitating equivalent quantities of sulphate of manganese and borax.

II. is obtained by using a slight excess of sulphate of manganese.

The loss on heating is mainly water, always increased, however, by the loss of some boric acid carried off by the water.

	I.	II.
Loss on heating	30.90	31.57
MnO	26.78	28.82
B_2O_3	42.36	39.69

To correspond to the formula $MnO.B_4O_6$, I. should have contained for the manganese present 52.8, and II. 56.8 per cent of boric acid. This is irrespective of the water always contained in the product and which in the pure salt is $5H_2O$. At one time it was thought possible that the loss of boric acid could be obviated by washing the precipitate with a saturated solution of boric acid in water, and even prepare the respective solutions of manganous chloride and borax with a saturated solution of boric acid, but this treatment was followed only by a considerable loss of precipitate without changing the composition to any extent.

Since the precipitation takes place in water, the precipitate has never the composition which might be expected from the reaction above referred to. The precipitate has then already suffered from dissociation, as I ascertained by removing the water and with it the salts as far as mechanical means allow, entirely avoiding washing, however, and then analyzing not

only the precipitate but the solution likewise. This takes place even when we try to produce a precipitate which contains 1 molecule of MnO for 1 molecule of B_2O_3, though not so marked; *i. e.*, dissociation decreases as the manganese increases in the precipitate, and this may be washed even without much loss of boric acid and hardly any loss of manganese. This precipitate keeps white while wet but darkens on drying.

There is but one product which possesses sufficient stability, and this is $MnO.B_4O_6 + 5H_2O$, which, however, may not be produced directly by precipitation. It can, however, be obtained by adding so much boric acid to wet precipitates, lacking boric acid, as the theory demands, and then allowing to dry spontaneously. Such mixtures dry white (rose) and remain so when dried even as high as 150° C. They are absolutely amorphous, which would not have been the case if the boric acid had not gone into combination. Even the microscope does not reveal any crystals. Heating with a little water in a sealed tube produces a granular mass. The formula of this compound is $MnB_4O_7 + 5H_2O$. At 120° C. it loses $2H_2O$.

Loss at 120° C.	Calculated.	Found.
$2H_2O$	11.98	12.04

The salt, however, is quite hygroscopic and should therefore be well dried over sulphuric acid under the air-pump. At temperatures above 120° C. the salt loses water gradually, but the rest of the water can be removed only at red heat, when some boric acid is also lost by being carried off by the water. The salt, therefore, colors by oxidation. It is quite dense and is evidently not well suited to be applied technically.

The salt $MnB_4O_7 + 3H_2O$, when finely ground and brought into contact with water, takes up again $2H_2O$, lost on drying, setting thereby like plaster of Paris.

Both hydrated salts yield their manganese readily to hot oils, producing quick-drying varnishes. The most convenient and economical method for the production of the salt consists in precipitating a borate of manganese of the approximate

composition, MnB_2O_4, using a solution of manganese chloride and a borax solution to which so much sodium hydroxide has been added as the borax already contains, then filtering, and washing rapidly with cold water free from air. In the solution the boric acid and manganese are determined, and from this it is easily possible to calculate the quantity of boric acid which should be added to the mass remaining upon the filter. Working under the same conditions, I should think that manufacturers, once for all, could determine such quantity of acid, especially as a slight excess of boric acid does not influence the nature of the dryers.

The analytical work is not onerous, since caustic soda decomposes the salt easily into manganous hydroxide and borate of sodium. The manganese in the precipitate is determined volumetrically by Volhard's method, while the boric acid is determined in the solution by means of the glycero-boric acid method.

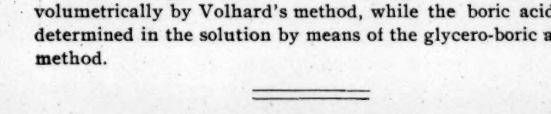
Contributions from the Sheffield Laboratory of Yale University.

C.—ON THE ACTION OF PHENYLHYDRAZINE ON BENZOYLPSEUDOTHIOUREAS: 1,5-DIPHENYL-3-AMINOPYRRO-α,β'-DIAZOLE DERIVATIVES.

By Henry L. Wheeler and Alling P. Beardsley.

It was stated in a previous article[1] that the acylpseudothioureas readily react with phenylhydrazine to form aminotriazoles, but the question whether the resulting aminotriazoles are 1,5-dialkyl-3-aminotriazoles (formula I.) or 1,3-dialkyl-5-amino derivatives (formula II.) was not decided at that time.

I.



[1] This Journal, 26, 411 (1901).

II. $C_6H_5CON=C(SCH_3)—NRR'$ / $H_2N———NHC_6H_5$ =

$$C_6H_5C—N=C—NRR' \quad + \quad H_2O$$
$$\| \qquad | \qquad\qquad\quad CH_3SH$$
$$N———NC_6H_5$$

It was shown that certain acylcarbamic, acylthiocarbamic, and acylimidothiocarbonic esters act with phenylhydrazine, forming triazole derivatives, and in these cases the relative tendency of the groups to react with the hydrogen of the amino group in phenylhydrazine could be expressed by the following arrangement:

$$CSAlk > CS > CO > COAlk.$$

That is to say, mercaptan is eliminated rather than hydrogen sulphide, and both these products more readily than water or alcohol, the latter appearing to have the least tendency to separate.[1] From this it would be expected that the triazoles formed from the benzoylpseudothioureas would be 1,5-diphenyl-3-aminotriazoles, the reaction taking place according to the first equation. This we have proved to be the case, as follows:

(*a*) When the product obtained from benzoylthiolmethylpseudothiourea, $C_6H_5CON=C(SCH_3)NH_2$, and phenylhydrazine was acted on by nitrous acid in concentrated hydrochloric acid, the amino group was replaced by chlorine, and the resulting compound appeared to be identical with the chlortriazole obtained by Cleve[2] from 1,5-diphenyloxytriazole. Cleve states that the chlorine derivative melts at 96°, while our product melted at 95° to 95°.5.

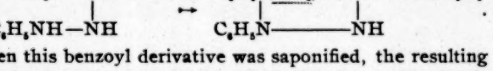
(*b*) The substance was shown conclusively to be a 1,5-diphenyltriazole by the following synthesis: Phenylaminoguanidine, in ether, was shaken with benzoyl chloride and alkali. This produced a dibenzoyl derivative which, on boiling in alcohol, separated water and gave 1,5-diphenyl-3-benzoylaminotriazole (III.):

[1] This JOURNAL, **27**, 258 (1902).
[2] Ber. d. chem. Ges., **29**, 2672.

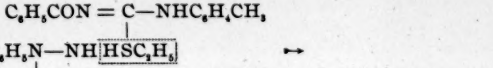
III.

When this benzoyl derivative was saponified, the resulting aminotriazole proved to be identical with the aminotriazole from the acylpseudothiourea and phenylhydrazine.

(*c*) The same benzoylaminotriazole was obtained from our aminotriazole and benzoyl chloride, and also by causing unsymmetrical benzoylphenylhydrazine to act on benzoyliminodiethyldithiocarbonate, and then boiling the resulting *a*-phenyl-*a*,*c*-dibenzoylthiolethylpseudothiosemicarbazide (IV.) with alcoholic ammonia.

IV. 

That the same reaction by which the aminotriazole is obtained from phenylhydrazine and the above benzoylpseudothiourea holds equally for the production of substituted aminotriazoles from substituted pseudothioureas, was proved by preparing the paratolyl derivative by the following method: Benzoylparatolylthiolethylpseudothiourea was warmed with unsymmetrical benzoylphenylhydrazine, whereupon mercaptan was eliminated and *a*,*c*-dibenzoyl-*c'*-paratolyl-*a*-phenylaminoguanidine (V.) was formed. When this was boiled with the calculated quantity of dilute alcoholic potash a benzoyl group was removed and water was split off, yielding 1,5-diphenyl-3-paratolylaminotriazole. This compound was found to be identical with the product obtained by Wheeler and Johnson from benzoylparatolylthiolethylpseudothiourea and phenylhydrazine.

V. 

As far as examined, the acylpseudothioureas conform to the rule above mentioned. The —NH_2 group of the phenylhydrazine attacks the mercapto group in preference to the CO group. The question whether the above rule applies in the case of other types of compounds that contain these groups, and give triazoles[1] or their analogues, will receive attention at a later time.

EXPERIMENTAL PART.

Benzoylthiolbenzylpseudothiourea, $C_6H_5CO—N = C(SCH_2C_6H_5)NH_2$.—Benzoylthiourea was dissolved in dilute potassium hydroxide and benzyl chloride was added, the mixture being subjected to violent agitation by a mechanical stirrer. After filtering, the resulting semisolid mass was crystallized from alcohol, whereupon it formed glistening white plates, insoluble in ether or benzene. It was soluble in hydrochloric acid and it melted at 161°. A nitrogen determination gave:

	Calculated for $C_{15}H_{14}ON_2S$.	Found.
N	10.37	9.94

1,5-Diphenyl-3-aminotriazole. — Molecular proportions of phenylhydrazine and benzoylthiolmethylpseudothiourea[2], or the above pseudothiourea, were heated on the water-bath, in benzene, for three or four hours. After the benzene had been evaporated the reaction-product was washed with ether and crystallized from alcohol. It formed colorless prisms, which melted at 154°.5. A nitrogen determination gave the following result:

	Calculated for $C_{14}H_{12}N_4$.	Found.
N	23.72	23.71

This aminotriazole is very difficultly soluble in water and cold benzene, readily in hot benzene and alcohol. From the latter solvent it separates in the form of prisms or striated plates. It is very stable, strong, boiling sulphuric acid or

[1] Certain acylphenylthioureas and acylphenylurethanes cannot be used to test this rule since they react abnormally, saponification taking place. J. Am. Chem. Soc., **22**, 368 (1900).

[2] Wheeler and Merriam: *Ibid.*, **23**, 293 (1901).

potash having no effect on the substance. Attempts to prepare the substance by heating 1,5-diphenyl-3-chlortriazole[1] or the mercaptotriazole, or the alkylmercaptotriazoles[2] with ammonia were without success.

It behaves in a manner peculiar to the aminotriazoles on attempting to diazotize in hydrochloric acid solution. The base was dissolved in concentrated hydrochloric acid and to the cold solution the calculated quantity of sodium nitrite was added. After the mixture had stood for several hours at 0°, crystals separated which, on purification by alcohol, melted at 95° to 95°.5 and appeared to be identical with the 1,5-diphenyl-3-chlortriazole described by Cleve.[3] A nitrogen determination gave :

	Calculated for $C_{14}H_{10}N_3Cl$.	Found.
N	16.43	16.42

The *picrate* forms intensely yellow, lozenge-shaped plates, on mixing alcoholic solutions of the constituents. It melts at 183°. A nitrogen determination gave :

	Calculated for $C_{20}H_{13}O_7N_7$.	Found.
N	21.11	21.43

The *hydrochloride* results when the aminotriazole is boiled in concentrated hydrochloric acid. On cooling, small, colorless plates separate, which melt at 205°, without effervescence, being distinguished by this from the benzoyl chloride addition-product, which melts at the same point, but with effervescence. A nitrogen determination gave :

	Calculated for $C_{14}H_{13}N_4Cl$.	Found.
N	20.55	20.52

1,5-Diphenyl-3-benzoylaminotriazole.—This was prepared by adding benzoyl chloride (1 molecule) to the aminotriazole (2 molecules) in warm benzene. Under these conditions the above hydrochloride separates and the benzoyl derivative remains in solution.

[1] Cleve : Ber. d. chem. Ges., **29**, 2672.
[2] This JOURNAL, **27**, 257 (1902).
[3] *Loc. cit.*

It can also be obtained from the benzoyl chloride addition-product, either by shaking with alkali and dissolving out the product with benzene, or by heating the substance to its melting-point, when hydrogen chloride is evolved, leaving the benzoyl derivative as a brittle resin. This crystallizes from dilute alcohol or from benzene and ligroin, and melts at 159° to 160°. A nitrogen determination gave :

	Calculated for $C_{21}H_{16}ON_4$.	Found.
N	16.47	16.39

Benzoylaminotriazole is readily soluble in benzene and alcohol. It is precipitated from its alcoholic solution by water. On evaporating its solutions on the steam-bath it forms a varnish. When treated with hydrochloric acid it is converted into a hydrochloride. This is identical with the benzoyl chloride addition-product described below.

The *sulphate* is produced when its alcoholic solution is allowed to evaporate at ordinary temperatures with dilute sulphuric acid. The resulting crystals, purified by dissolving in alcohol and precipitating with ether, melted at 195°.

The Hydrochloride or Benzoyl Chloride Addition-product.— When the aminotriazole was warmed in an excess of benzoyl chloride without a solvent, on the steam-bath, it dissolved and then suddenly precipitated out as a solid cake. This was washed with benzene, in which it is insoluble, and crystallized from alcohol. It formed bunches of small, colorless plates, which melted at 205° with effervescence. A nitrogen determination gave :

	Calculated for $C_{21}H_{17}ON_4Cl$.	Found.
N	14.87	15.07

1,5-Diphenyl-3-acetylaminotriazole Hydrochloride. — When acetyl chloride was added to the aminotriazole, vigorous action took place. A viscous paste was immediately formed, which was gradually changed to a white powder by boiling with the chloride. This, on washing with benzene, melted at 156° to 157°, and was analyzed with the following result :

	Calculated for $C_{16}H_{13}ON_4Cl$.	Found.
N	17.80	17.71

The constitution of the triazole derivatives just described was determined by the two following syntheses:

I. a,c-Dibenzoyl-a-phenylaminoguanidine, $C_6H_5N(COC_6H_5)$—NH—C(NH)—$NHCOC_6H_5$.—Phenylaminoguanidine[1] (6 grams) and benzoyl chloride were added to 200 cc. of dilute sodium hydroxide, covered with ether, with vigorous shaking. As soon as an excess of benzoyl chloride was evident from its odor, the precipitate was filtered and washed with water and ether. The yield was 8.5 grams. This material could not be crystallized unaltered from alcohol. As obtained above, possessing every appearance of purity, it melted with effervescence at 156°, and a nitrogen determination gave:

	Calculated for $C_{21}H_{18}O_2N_4$.	Found.
N	15.64	15.50

When this compound was boiled for six hours in absolute alcohol, it was dehydrated, 1,5-diphenyl-3-benzoylaminotriazole resulting. To the alcoholic solution of the last, strong hydrochloric acid was added and the boiling continued. The benzoyl group was thus removed and the hydrochloride of 1,5-diphenyl-3-aminoguanidine formed, from which the free base was obtained by alkali. This product and that from the action of phenylhydrazine on the benzoylpseudothioureas were identical.

II. a-Phenyl-a,c-dibenzoylthiolethylpseudothiosemicarbazide, $C_6H_5N(COC_6H_5)NH$—$C(SC_2H_5)$=$NCOC_6H_5$. — When 4 grams of *a*-benzoyl-*a*-phenylhydrazine and 4 grams of benzoylimidodithiodiethyl carbonate[2] were warmed in alcohol, mercaptan was evolved. Evaporation of the alcohol left a varnish which crystallized from benzene in square plates, melting at 170° to 171°. When pure it is difficultly soluble in alcohol. A nitrogen determination gave:

[1] Pellizzari: Gaz. chim. ital., 21, 333.

[2] This compound and the analogous imidodimethyl carbonate were described as carbamates, owing to a typographical error in the manuscript. J. Am. Chem. Soc., 23, 292 (1901).

	Calculated for $C_{29}H_{21}O_2N_3S$.	Found.
N	10.42	10.37

This material was boiled with alcoholic ammonia, whereupon it very slowly dissolved and mercaptan was evolved, and there was formed, as an intermediate product, *a*-phenyl-*a*,*c*-dibenzoylaminoguanidine. The latter, however, under the conditions of the experiment, eliminated water, becoming 1,5-diphenyl-3-benzoylaminotriazole. Hydrogen chloride was passed into the benzene solution and the precipitate thus produced was crystallized from alcohol and proved identical with the benzoyl chloride addition-product described above.

1,5-Diphenyl-3-phenylaminotriazole.—This was prepared by warming benzoylphenylthiolethylpseudothiourea,

$$C_6H_5CONHC(SC_2H_5) = NC_6H_5,^1$$

on the steam-bath with the molecular proportion of phenylhydrazine. After three or four hours' heating, mercaptan had ceased coming off and the product had solidified. The residue was crystallized from alcohol from which it appears in fine, white needles, melting at 202°. A nitrogen determination gave :

	Calculated for $C_{20}H_{16}N_4$.	Found.
N	17.94	17.99

Phenylaminotriazole does not form a hydrochloride, either when treated with hydrochloric acid or when hydrogen chloride is passed into its solution in benzene. It may be boiled for hours with strong alkali with no effect. It could not be prepared from the chlortriazole or the mercaptotriazoles by heating with aniline.

1,5-Diphenyl-3-benzoylphenylaminotriazole is formed when phenylaminotriazole is heated with benzoyl chloride on the water-bath. The reaction-product, crystallized from dilute alcohol, appears in compact, ill-formed crystals, which are very soluble in benzene and insoluble in ligroin. It was found to melt at 148° to 149° and a nitrogen determination gave :

[1] J. Am. Chem. Soc., 23, 293 (1901).

	Calculated for $C_{27}H_{20}ON_4$.	Found.
N	13.46	13.60

1,5-Diphenyl-3-paratolylaminotriazole.—This has been prepared by Wheeler and Johnson[1] from benzoylparatolylthiolethylpseudothiourea and phenylhydrazine. The following process leads to the same compound: Molecular quantities of *a*-benzoyl-*a*-phenylhydrazine and benzoylparatolylthiolethylpseudothiourea were warmed in alcohol on the steam-bath. Mercaptan came off slowly and after long heating the material solidified. It was difficultly soluble in alcohol, and formed long, colorless needles which melted at 279° with effervescence. The material was free from sulphur, and a nitrogen determination agreed with the calculated for *a*,*c*-dibenzoyl-*c'*-paratolyl-*a*-phenylaminoguanidine:

	Calculated for $C_{28}H_{24}O_2N_4$.	Found.
N	12.5	12.8

This substance was boiled with dilute alcoholic potash, whereupon, in about a half hour, beautiful, colorless, minute, stout crystals separated which melted at 227° to 228°. This material proved identical with the paratolylaminotriazole previously prepared, but to which the melting-point 225° to 226° was assigned.

Benzoylmethylphenylthiolmethylpseudothiourea, $C_6H_5CON = C(SCH_3)NCH_3C_6H_5$.—Molecular quantities of benzoylimidodithiodimethyl carbonate and monomethylaniline were heated in benzene, on the water-bath, for three or four hours. After evaporating the benzene the product was washed with ether and crystallized from alcohol. It formed colorless prisms melting at 113°. A nitrogen determination gave:

	Calculated for $C_{18}H_{18}ON_2S$.	Found.
N	9.86	9.90

1,5-Diphenyl-3-methylphenylaminotriazole.—Benzoylmethylphenylthiolmethylpseudothiourea was dissolved in a mixture of benzene and alcohol, exactly one molecular proportion of

[1] This JOURNAL, **26**, 414 (1901).

phenylhydrazine added, and the mixture allowed to stand in the cold. After several days a few crystals had separated. The mother-liquor was found to contain only unaltered material. The crystals were purified by alcohol, in which they are extremely insoluble. They formed lozenge-shaped plates which melted with effervescence at 202° to 203°, after showing signs about 5° lower. The material was free from sulphur, and nitrogen determinations gave the following results:

	Calculated for $C_{21}H_{18}N_4$	Found. I.	II.
N	17.18	16.84	16.89

NEW HAVEN, CONN., Nov., 1902.

SEPARATION OF LEAD FROM MANGANESE BY ELECTROLYSIS.

BY A. F. LINN.

In its chemical properties manganese very closely resembles iron, but on electrolysis it behaves more like lead. Neumann[1] has described a method for the separation of lead and manganese, by the current, in the presence of 20 per cent of free nitric acid, at a temperature between 60° and 70° C. The current density was 1.5 to 2 amperes and the electromotive force 2.5 to 2.7 volts. The method yields only approximately accurate results when carried out as described, and when the amount of manganese does not exceed 0.03 gram for 150 cc. of the electrolyte. If the amount of manganese exceeds 0.03 gram, or if the deposition continues too long, the lead peroxide deposit is no longer free from the other metal. In a former paper[2] I have shown that lead can be completely deposited from a solution of its phosphate in an excess of phosphoric acid. The similarity of lead to manganese, referred to above, led me to try the current on a manganese solution under like conditions. No deposit whatever was obtained, even after prolonged action of the current. The solution, however, acquired the pink color usually produced in acid solutions of manganese, and mentioned by Neumann[3] and also by

[1] Chem. Ztg., 1896, No. 39, p. 20.
[2] J. Am. Chem. Soc., 24, 435.
[3] "Electrolytic methods of analysis."

Experimental Results.

No.	Lead taken.	Lead found.	Difference.	N. D$_{100}$.	Voltage.	Hours.	Dilution.	H_3PO_4.	Manganese.
	Gram.	Gram.	Per cent.	Ampere.			cc.	cc.	Gram.
1	0.1000	0.1001	+0.10	0.005	2.75	22	130	13	0.05
2	0.1000	0.0998	−0.20	0.004	"	24	"	13	"
3	0.0344	0.0344	....	0.005	2.57	21	"	10	"
4	"	0.0343	−0.29	"	"	17	"	10	"
5	"	0.0344	....	"	2.50	22	"	7	"
6	0.1000	0.0997	−0.30	0.006	2.6	17	"	14	"
7	0.0625	0.0622	−0.48	0.005	"	"	"	10	"
8	0.0750	0.0755	+0.66	"	2.7	"	"	10	"
9	0.0613	0.0618	+0.80	0.003	2.3	"	"	12	"
10	0.1000	0.0998	−0.20	0.005	2.6	18	"	14	0.10

Smith.[1] This difference of deportment toward the current suggested a method of separation. The preliminary trials showed that the lead was completely deposited on the cathode as metal, but that it enclosed a small amount of manganese. Further work has shown that under different conditions a perfect separation is possible. The method of working is similar to that employed when lead alone is present. To a definite amount of lead and manganese, in solution as nitrates, is added sodium hydrogen phosphate, slightly more than sufficient for complete precipitation. The phosphates are then dissolved in an excess of pure phosphoric acid solution (sp. gr. 1.70), and the solution acted on by a current of known strength. The deposit of lead is rapidly washed with cooled, freshly-boiled distilled water, absolute alcohol and ether, dried at 100° to 110° C. in the air-bath, and weighed. The amounts of lead and manganese should not exceed 0.1 gram each for 130 cc. of the electrolyte. The time required for this amount is sixteen to seventeen hours. The time can be shortened by increasing the current density, but in that case the deposit is spongy and seems to be very rapidly soluble in the wash-water. If the lead exceeds 0.1 gram there are apt to be found on the cathode, at certain places, patches of needle-like crystals of lead. All the results recorded above were obtained at ordinary temperatures. Application of heat (60° to 70° C.) retards instead of hastens the deposition of the lead. In each experiment made a small amount of the hydrated peroxide of manganese formed upon the anode. In most instances the color of this deposit was brown, but in a few cases it had a decidedly copper-red appearance.

A portion of this work was carried out in the laboratory of the University of Michigan.

I desire here to acknowledge my indebtedness to Professor Prescott and to Drs. Gomberg, Campbell, and Sullivan for courtesies received.

WITTENBERG COLLEGE, SPRINGFIELD, O., Sept. 9, 1902.

[1] This JOURNAL, 8, 208.

REVIEWS.

ENZYMES AND THEIR APPLICATIONS. By DR. JEAN EFFRONT. English translation, by SAMUEL C. PRESCOTT, S.B. New York: John Wiley & Sons. 322 + xi pp.

The important discovery of zymase by Buchner in 1897, together with the remarkably interesting results reached by Fischer in the study of the influence of stereoconfiguration on the action of enzymes, and the important researches of Croft Hill on reversible zymohydrolysis have served to awaken a new interest in the chemistry of zymotic processes during the last few years. Some evidence of this increased activity in this field is furnished by the fact that during the last few years no less than three comprehensive works on this subject have appeared. These are the following: "The Soluble Ferments and Fermentation," by J. Reynolds Green; "Die Fermente und ihre Wirkungen," by Carl Oppenheimer; and "Les Enzymes et leurs Applications," by J. Effront. An English translation of this last work is now at hand. The French edition of Effront's book has enjoyed a wide reputation. In its original form the book is divided into two parts. Part I. deals with the enzymes of the carbohydrates, and the oxidases, and their practical application in the industrial arts. Part II. is still in preparation and will have to deal with the proteolytic enzymes and the toxins. It has been the aim of the translator to render "available in English the valuable material contained in the original French edition."

Taken as a whole the book, both in the original and in the translation, has much to recommend it to persons interested in the subject of fermentation. It gives us a readable and intelligible account of the enzymes of the carbohydrates and fats, and the oxidases. It treats of their discovery, occurrence, and distribution in nature, the methods of preparation, and their properties. It describes the chemical changes produced by these enzymes and gives the laws and conditions governing their mode of action. Generally speaking, the author inclines to the practical side of the subject, and it is in such portions of the book especially that one finds a great many hints and suggestions of value. About one-fourth of the book is devoted to the consideration of diastase (amylase). At first thought it might seem that too much space had been set apart for the consideration of this enzyme in a work of this size. On the other hand, when we consider the great historical interest attaching to this enzyme, its wide distribution in the vegetable and animal kingdom, its important rôle in

metabolism, and its great application in the brewing industry, it is perhaps not too much after all. The author inclines, and rightly too, I think, to the French nomenclature, first proposed by Duclaux, whereby the enzyme takes the ending ASE, and is named, whenever it is possible to do, after the substance on which its action was first observed. In the main, this system of nomenclature has been adhered to both in the original and in the translation, and yet, in both, the somewhat antiquated name of steapsin for the fat-splitting enzyme is frequently used. The value of the book has been considerably increased by putting the chapter contents at the beginning of each chapter, and by a comprehensive bibliography which, for the sake of convenience, has been subdivided and placed at the end of each chapter, or in some cases at the end of certain general or special topics. In these several bibliographies a decided leaning to the French literature of the subject is observable. If this is a fault it is certainly not an unnatural one in a French author, and in some respects it is a good one, for the reason that he has gotten together in available form all of the more important references to the work of the French school on this subject. On the other hand, the book is no mere compilation. One can easily see that it has been written by a worker and a doer in this field, and after all, this is perhaps its strongest point.

The translation of the work by Prescott has been made in the spirit of the original, and will doubtless prove serviceable to American chemists and physiologists.

It is not intended to convey the idea, however, that either the original or the translation is altogether free from faults and mistakes. Both show typographical errors, for some of which the publishers, for others the author and translator are responsible, and in both the original and the translation there has been observed an occasional looseness and carelessness of expression which tend to confuse the reader and which, with a little pains, could have been avoided. Thus, under the head of Emulsin in the original, page 311, one finds this sentence :

" L'émulsine, qui agit sur des corps très différents au point de vue chimique, agit différemment sur les divers glucoses, d'après leur configuration."

Here the word glucoses is used for glucosides. In the translation this sentence is rendered thus :

" Emulsin, which acts on bodies very differently from a chemical point of view, acts differently on the various monosaccharides, according to their configuration."

It will be observed that the error in the original is repeated

in the translation, and that in addition to this a mistake occurs in the translation itself. Taken together, these two mistakes have robbed an important sentence entirely of its meaning. Then again, the constant use of the word diastase as a general name for enzyme is scarcely warranted by the best English usage. The word diastase, meaning enzyme, is good French, but this does not make it good English.

Similarly, the use of the words "hydration" and "hydrating," in lieu of hydrolysis and hydrolyzing, should not be allowed to pass unnoticed. The processes of hydration and hydrolysis are altogether different from a chemical point of view. Both apparently involve the direct union of water and the substance acted on. In the process of hydration, however, as this term is ordinarily employed, the action stops at this point, whereas in hydrolysis a subsequent decomposition of the complex molecule occurs with the production of one or more simpler substances. As the enzymes seem to be primarily concerned in bringing about just such decompositions, through the agency of water, it would seem better to still hold to the word hydrolysis, and certainly there is nothing to be gained in calling the process hydration. These are doubtless minor errors, but like the spelling of Fischer's name Fische in the original, and Bunsen's Bunzen in both the original and in the translation, they nevertheless serve to detract somewhat from the merits of the publication. J. H. K.

DIE ZEHRSETZUNG STICKSTOFFFREIER ORGANISCHER SUBSTANZEN DURCH BAKTERIEN. Von. DR. O. EMMERLING, Privatdozent an der Universität Berlin. Mit sieben Lichtdrucktafeln. Braunschweig: Druck and Verlag von Friedrich Vieweg und Sohn. 1902. 141 pp.

This little monograph arose from a series of lectures which the author delivered to chemists on bacterial fermentations. It is intended to give, briefly, details which cannot be taken up in the lectures. He first takes up fermentations which result in oxidation, beginning with the acetic acid fermentation. The lactic acid fermentation is next considered and attention is called to its importance in agriculture and in the arts. The butyric acid and the butyl alcohol fermentations, as well as the fermentation of cellulose, are also fully considered. The book contains much information concerning the chemical decompositions of nitrogen-free organic matter brought about by bacteria, and will undoubtedly be of much service to those interested in this field of work. Two excellent methods for the preparation of lactic acid and dioxyacetone by means of bac-

teria are given by the author, which are not found in any book on organic chemistry. The book contains a good index and seven tables of microphotographs of bacteria. W. R. O.

JAHRESBERICHT ÜBER DIE FORTSCHRITTE DER CHEMIE UND VERWANDTER THEILE ANDERER WISSENSCHAFTEN. Begründet von J. LIEBIG und H. KOPP; unter Mitwirkung namhafter Fachgenossen herausgegeben von G. BODLÄNDER, W. KERP, und G. MINUNNI. Für 1894. Viertes Heft. Fünftes Heft. Braunschweig: Vieweg. 1902.

The old Jahresbericht comes slowly along, and it appears to be running a hopeless race. The fourth and fifth numbers for the year 1894 have recently been issued, and will of course be welcome. It would be cruel to complain of the delay in the preparation of this valuable work. The task is almost superhuman, and chemists may be thankful if they get for any year this complete record of the work done by chemists. How the editors and publishers are ever to make up the arrears of eight years it is hard to say. They have been trying to do so for many years past. Editors come and editors go. It is to be hoped that Liebig's Jahresbericht will go on forever. I. R.

Corrections.

As the corrected proof of the article by S. F. Acree and J. E. Hinkins on the "Hydrolysis of Triacetylglucose by Enzymes" was not returned to the editor until after the time for publication of the November number of this JOURNAL, the following changes are to be made:

Page 370, line 34, for *guickly* read *quickly*.
" 371, " 14, " *emulsion, diastase, etc., can be* read *emulsin, and diastase, can be*.
Page 371, line 32, for *1 liter, and which was the N/11.51 acid* read *1 liter, which was N/11.51 acid*.
Page 372, line 27, place comma after *instance*.
" 375, " 36, " semicolon after *vary*.
" 380, last line, for *N/50* read *N/40*.
" 384, line 14, for *0.85* read *0.83*.
" " " 26, insert *5.00* at the space ....
" " " 30, for *N/28—0.58* read *N/29—0.60*.
" 385 " 28, " *0.68* read *0.67*.
" " " 35, " *N/39* " *N/39.50*.
" " " 38, " *7.90* read *7.00*.